ADVANCED INORGANIC CHEMISTRY

Fifth Edition

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*. . . Chemistry, the most cosmopolitan of sciences,
the most secret of arts.*
D'Arcy Wentworth Thompson

La Chimie crée son objet.
Marcellin Berthelot

CIPLES

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·, Vol. 1, Pergamon Press, Oxford, 1987.
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Chapter Two

Introduction to Ligands and Complexes

GENERAL REMARKS

2-1. Introduction

It was known long before the Danish chemist S. M. Jørgensen (1837–1914) began his extensive studies on the synthesis of such "complex" compounds that the metal halides and other salts could give compounds with neutral molecules and that many of these compounds could easily be formed in aqueous solutions. The recognition of the true nature of "complexes" began with Alfred Werner (1866–1919) as set out in his classic work *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie* (1905)[1]; he received the Nobel Prize for this work in 1913. Werner showed that neutral molecules were bound directly to the metal so that complex salts such as $CoCl_3 \cdot 6NH_3$ were correctly formulated $[Co(NH_3)_6]^{3+}Cl_3^-$. He also demonstrated that there were profound stereochemical consequences of the assumption that the molecules or ions (ligands) around the metal occupied positions at the corners of an octahedron or a square. The stereochemical studies of Werner were later followed by the ideas of G. N. Lewis and N. V. Sidgwick, who proposed that a chemical bond required the sharing of an electron pair. This led to the idea that a neutral molecule with an electron pair (Lewis base) can donate these electrons to a metal ion or other electron acceptor (Lewis acid). Well-known examples are the following:
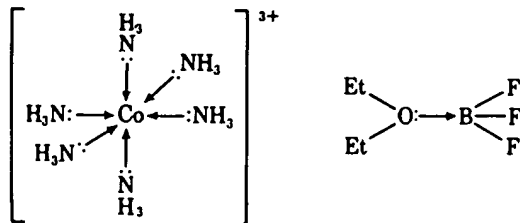
[1]Braunschweig, 1905; English translation of second edition as *New Ideas on Inorganic Chemistry*, by E. P. Hedley, London, 1911.

We can now define a *ligand** as any molecule or ion that has at least one electron pair that can be so donated. Ligands may also be called Lewis bases; in the terms used in organic chemistry, they are nucleophiles. Metal ions or molecules such as BF_3 with incomplete valence electron shells are Lewis acids or electrophiles.

Although it is possible to regard even covalent compounds from the donor–acceptor point of view—for example, we could regard methane (CH_4) as composed of C^{4+} and four H^- ions—it is not a particularly profitable or realistic way of looking at such molecules. Nevertheless, in inorganic chemistry, ions such as H^-, F^-, Cl^-, NO_3^-, and SO_4^{2-}, and groups such as CH_3^- and $C_6H_5^-$, are commonly termed ligands even when they are bound in simple molecules by largely covalent bonds as in SF_6 or $W(CH_3)_6$. Although SiF_4 is normally called a molecule and SiF_6^{2-} a complex anion, the nature of the Si—F bonds in each species is essentially the same.

There are many ways of classifying ligands. One approach is based on the type of bonding interaction between the central atom and its neighbors. The bonding details are dealt with later, but the distinction between two major types of ligand can be illustrated by posing two questions.

1. Why do molecules like water or ammonia give complexes with ions of *both* main group and transition metals—for example, $[Al(OH_2)_6]^{3+}$ or $[Co(NH_3)_6]^{3+}$, while other types of molecules such as PF_3 or CO give complexes only with transition metals?

2. Although PF_3 and CO give neutral complexes such as $Ni(PF_3)_4$ or $Cr(CO)_6$, why do NH_3, amines, oxygen compounds, and so on, not give complexes such as $Ni(NH_3)_4$?

There are two main classes of ligands:

(*a*) *Classical* or *simple donor ligands* act as electron-pair donors to acceptor ions or molecules, and form complexes with all types of Lewis acids, metal ions, or molecules.

(*b*) *Nonclassical ligands, π-bonding* or *π-acid ligands,* form compounds largely if not entirely with transition metal atoms. This interaction occurs because of the special properties of both metal and ligand. The metal has *d* orbitals that can be utilized in bonding; the ligand has not only *donor* capacity but also has *acceptor* orbitals. This latter distinction is perhaps best illustrated by comparison of an amine, $:NR_3$, with a tertiary phosphine, $:PR_3$. Both can act as bases toward H^+, but the P atom differs from N in that it has vacant 3*d* orbitals of low energy, whereas in N the lowest energy *d* orbitals are at far too high an energy to use. Another example is that of CO, which has no measurable basicity to protons, yet readily reacts with metals like nickel that have high heats of atomization to give compounds like $Ni(CO)_4$.

Ligands may also be classified electronically, that is, according to the number of electrons that they contribute to a central atom when these ligands are regarded (sometimes artificially) as neutral species. Thus atoms or groups that can form a covalent bond are regarded as *one-electron* donors—examples

*For a history of the term, see W. H. Brock *et al., Polyhedron,* 1983, **2**, 1.

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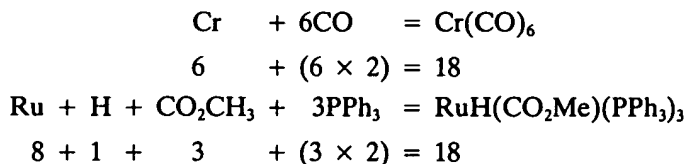are F, SH, and CH_3. Any compound with an electron pair is a *two-electron donor* (e.g., :NH_3, H_2O:). Groups that can form a single bond and at the same time donate can be considered to be *three-electron donors*. For example, the acetate ion can be either a one- or a three-electron donor, namely,

$$M-\ddot{O}-\overset{\overset{\displaystyle O}{\|}}{C}CH_3 \quad \text{or} \quad M\overset{O}{\underset{O}{<}}C-CH_3$$
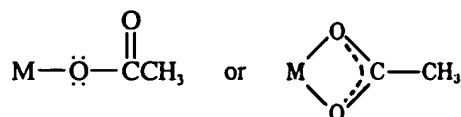
A molecule with two electron pairs (e.g., $H_2NCH_2CH_2NH_2$) can be regarded as a *four-electron donor,* and so on. This classification method is useful in that it is an aid in electron counting, particularly for transition metal complexes whose valence shells contain 18 electrons and whose stoichiometries correspond to what is called the *18-electron rule* or noble gas formalism. This is merely a phenomenological way of expressing the tendency of a transition metal atom to use all its valence orbitals, namely, the five nd, the $(n + 1)s$, and the three $(n + 1)p$ orbitals as fully as possible in metal-ligand bonding. The sum of the number of valence electrons in the gaseous atom plus the number of electrons from neutral ligands may attain a maximum value of 18.

This is illustrated by the following examples:

$$Cr \quad + 6CO \quad = Cr(CO)_6$$
$$6 \quad + (6 \times 2) = 18$$
$$Ru + H + CO_2CH_3 + \quad 3PPh_3 \quad = RuH(CO_2Me)(PPh_3)_3$$
$$8 + 1 + \quad 3 \quad + (3 \times 2) = 18$$

A third way of classifying ligands is *structurally,* that is, by the number of connections they make to the central atom. Where only one atom becomes closely connected (bonded) the ligand is said to be *unidentate* [e.g., the ligands in $Co(NH_3)_6^{3+}$, $AlCl_4^-$, $Fe(CN)_6^{3-}$]. When a ligand becomes attached by two or more atoms it is *bidentate, tridentate, tetradentate,* and so on, generally multidentate. Note that the Greek-derived corresponding prefixes (mono, ter, poly, etc.) are also used in the literature.

Bidentate ligands when bound entirely to one atom are termed *chelate,* as in (2-I), (2-II), and (2-III).
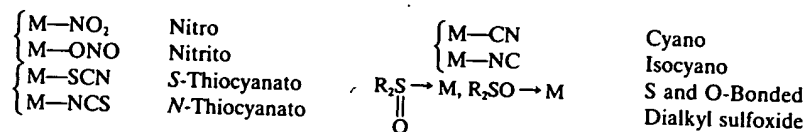

$$(2\text{-I}) \qquad (2\text{-II}) \qquad (2\text{-III})$$
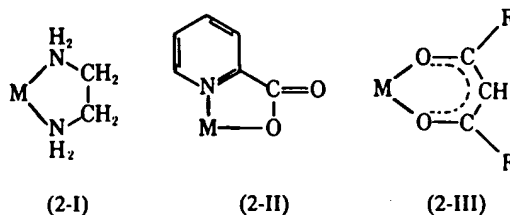
Another important role of ligands is as *bridging groups.* In many cases they serve as *unidentate* bridging ligands. This means that there is only *one*

ligand atom that forms two (or even three) bonds to different metal atoms. For monoatomic ligands, such as the halide ions, and those containing only one possible donor atom, this *unidentate* form of bridging is, of course, the only possible one. A few examples are shown in (2-IV) to (2-VI). Ligands having more than one atom that can be an electron donor often function as *bidentate* bridging ligands. Examples are shown in (2-VII) and (2-VIII).

(2-IV)   (2-V)   (2-VI)   (2-VII)   (2-VIII)
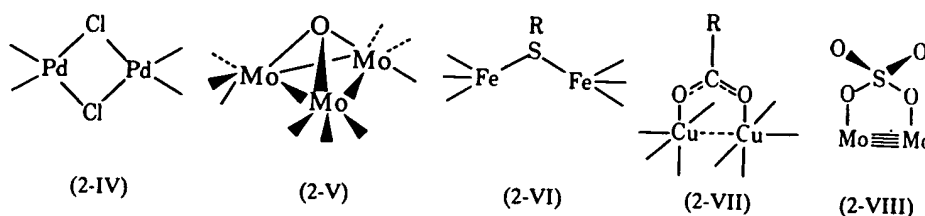
The standard notation for bridging ligands employs the descriptors η (eta) and μ (mu). The prefix η^n indicates that a ligand is using n of its atoms to form bonds to metal atoms (η is used also for nonbridging ligands, see Sections 2-10 to 2-12.), while the prefix μ implies that a ligand bridges two metal atoms. If a ligand bridges three, four, or more metal atoms, μ_3, or μ_4, and so on, are used. For example, in (2-IV), the chlorine atoms are μ-Cl, while in (2-V) the oxygen atom is μ_3-O. In (2-VII), the carboxylato ligand is μ,η^2 since it bridges two metal atoms (hence μ) employing two different oxygen atoms (hence η^2).

Some unidentate ligands have two or more different donor sites so that the possibility of *linkage isomerism* arises. Some important ligands of this type, which are called *ambidentate ligands*, are

$$\begin{cases} M{-}NO_2 \\ M{-}ONO \\ M{-}SCN \\ M{-}NCS \end{cases} \begin{matrix} \text{Nitro} \\ \text{Nitrito} \\ S\text{-Thiocyanato} \\ N\text{-Thiocyanato} \end{matrix} \qquad \begin{cases} M{-}CN \\ M{-}NC \end{cases} \begin{matrix} \text{Cyano} \\ \text{Isocyano} \end{matrix}$$

$R_2S \rightarrow M, R_2SO \rightarrow M$ S and O-Bonded
$\underset{O}{\overset{\|}{}}$ Dialkyl sulfoxide

The next sections discuss primarily the chemistry of simple donor ligands. Much of this chemistry applies equally well to main group metal ions (e.g., Na^+, Ca^{2+}, Ga^{3+}, or Cd^{2+}) and to transition metal ions. It is a chemistry largely of aqua ions, nitrogen donor ligands, such as ammonia or ethylenediamine, and halide ions, and it is chemistry of metal ions in positive oxidation states, usually 2+ and 3+.

Later sections consider complexes that have π-bonding ligands and also compounds that are called π *complexes,* which are those formed by unsaturated organic molecules. This is a chemistry largely of transition metals, often in formally low oxidation states such as -1, 0, and $+1$.

The borderline between π-bonding and non-π-bonding ligands is by no means clearly defined. Also the terms "nonclassical" versus "classical" are

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own in (2-IV) to (2-VI). Ligands
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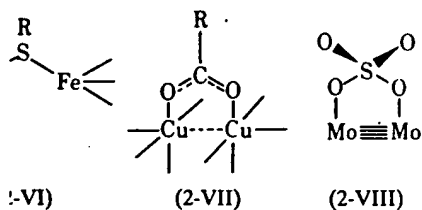
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. R₂SO → M	S and O-Bonded Dialkyl sulfoxide

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of limited validity, since Werner and his contemporaries studied complexes
of cyanide ion and of tertiary phosphines; even pyridine, which they used
extensively, is not solely a simple donor.

STABILITY OF COMPLEX IONS IN AQUEOUS SOLUTION

2-2. Aqua Ions

In a fundamental sense metal ions simply dissolved in water are already
complexed—they have formed aqua ions. The process of forming in aqueous
solution what we more conventionally call complexes is really one of displacing
one set of ligands, which happen to be water molecules, by another set. Thus
the logical place to begin a discussion of the formation and stability of complex
ions in aqueous solution is with the aqua ions themselves.

From thermodynamic cycles the enthalpies of plunging gaseous metal ions
into water can be estimated and the results, 2×10^2 to 4×10^3 kJ mol^{-1} (see
Table 2-1), show that these interactions are very strong indeed. It is of im-
portance in understanding the behavior of metal ions in aqueous solution to
know how many water molecules each of these ions binds by direct metal-
oxygen bonds. To put it another way, if we regard the ion as being an aqua
complex $[M(H_2O)_x]^{n+}$, which is then further and more loosely solvated, we
wish to know the coordination number x and also the manner in which the
x water molecules are arranged around the metal ion. Classical measurements
of various types—for example, ion mobilities, apparent hydrated radii, en-
tropies of hydration—fail to give such detailed information because they
cannot make any explicit distinction between those water molecules directly
bonded to the metal—the x water molecules in the inner coordination sphere—
and additional molecules that are held less strongly by hydrogen bonds to the
water molecules of the inner coordination sphere. There are, however, ways
of answering the question in many instances, ways depending, for the most

TABLE 2-1
Enthalpies of Hydration^a of Some Ions (kJ mol^{-1})

H⁺	−1091	Ca²⁺	−1577	Cd²⁺	−1807
Li⁺	−519	Sr²⁺	−1443	Hg²⁺	−1824
Na⁺	−406	Ba²⁺	−1305	Sn²⁺	−1552
K⁺	−322	Cr²⁺	−1904	Pb²⁺	−1481
Rb⁺	−293	Mn²⁺	−1841	Al³⁺	−4665
Cs⁺	−264	Fe²⁺	−1946	Fe³⁺	−4430
Ag⁺	−473	Co²⁺	−1996	F⁻	−515
Tl⁺	−326	Ni²⁺	−2105	Cl⁻	−381
Be²⁺	−2494	Cu²⁺	−2100	Br⁻	−347
Mg²⁺	−1921	Zn²⁺	−2046	I⁻	−305

^{a}Absolute values are based on the assignment of −1091 ± 10 kJ mol^{-1} to H⁺ (cf. H. F.
Halliwell and S. C. Nyburg, *Trans. Faraday Soc.*, 1963, **59**, 1126). Each value probably has an
uncertainty of at least $10n$ kJ mol^{-1}, where n is the charge of the ion.

part, on modern physical and theoretical developments. A few illustrative examples will be considered here.

For the transition metal ions, the spectral and, to a lesser degree, magnetic properties depend on the constitution and symmetry of their surroundings. For example, the Co^{II} ion forms both octahedral and tetrahedral complexes. Thus we might suppose that the aqua ion could be either $[Co(H_2O)_6]^{2+}$ with octahedral symmetry, or $[Co(H_2O)_4]^{2+}$ with tetrahedral symmetry. It is found that the spectrum and the magnetism of Co^{II} in pink aqueous solutions of its salts with noncoordinating anions such as ClO_4^- or NO_3^- are very similar to the corresponding properties of octahedrally coordinated Co^{II} in general, and virtually identical with those of Co^{II} in such hydrated salts as $Co(ClO_4)_2 \cdot 6H_2O$ or $CoSO_4 \cdot 7H_2O$ where from X-ray studies octahedral $[Co(H_2O)_6]^{2+}$ ions definitely exist. Complementing this, the spectral and magnetic properties of the many known tetrahedral Co^{II} complexes, such as $[CoCl_4]^{2-}$, $[CoBr_4]^{2-}$, $[Co(NCS)_4]^{2-}$, and $[py_2CoCl_2]$, which are intensely green, blue, or purple, are completely different from those of Co^{II} in aqueous solution. Thus there is little doubt that aqueous solutions of otherwise uncomplexed Co^{II} contain predominantly* well-defined, octahedral $[Co(H_2O)_6]^{2+}$ ions, further hydrated, of course. Evidence of similar character can be adduced for many of the other transitional metal ions. For all the di- and tripositive ions of the first transition series, the aqua ions are octahedral $[M(H_2O)_6]^{2(or\ 3)+}$ species, although in those of Cr^{II}, Mn^{III}, and Cu^{II} there are definite distortions of the octahedra because of the Jahn–Teller effect.† Information on aqua ions of the second and third transition series, of which there are only a few, however, is not so certain. It is probable that the coordination is octahedral in many, but higher coordination numbers may occur. For the lanthanide ions, $M^{3+}(aq)$, it is certain that the coordination number is higher.

For ions that do not have partly filled d shells, evidence of the kind mentioned is lacking, since such ions do not have spectral or magnetic properties related in a straightforward way to the nature of their coordination spheres. We are therefore not sure about the state of aquation of many such ions, although nmr and other relaxation techniques have now supplied some such information. It should be noted that, even when the existence of a well-defined aqua ion is certain, there are vast differences in the average length of time that a water molecule spends in the coordination sphere, the so-called mean residence time. For Cr^{III} and Rh^{III} this time is so long that when a solution of $[Cr(H_2O)_6]^{3+}$ in ordinary water is mixed with water enriched in ^{18}O, many hours are required for complete equilibration of the enriched solvent water with the coordinated water. From a measurement of how many molecules of H_2O in the Cr^{III} and Rh^{III} solutions fail immediately to exchange with the enriched water added, the coordination numbers of these ions by water were shown to be 6. These cases are exceptional, however. Most other

*However, there are also *small* quantities of tetrahedral $[Co(H_2O)_4]^{2+}$; see T. J. Swift, *Inorg. Chem.*, 1964, **3**, 526.

†This effect requires molecules to adopt geometries that do not lead to a degeneracy in valence level orbitals.

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aqua ions are far more labile, and a similar equilibration would occur too rapidly to permit the same type of measurement. This particular rate problem is only one of several that are discussed more fully in Section 29-3.
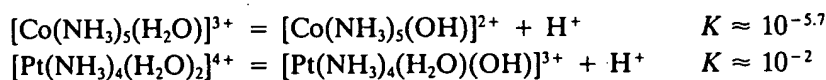
Aqua ions are all more or less acidic; that is, they dissociate in a manner represented by the equation

$$[M(H_2O)_x]^{n+} = [M(H_2O)_{x-1}(OH)]^{(n-1)+} + H^+$$

$$K_A = \frac{[H^+][M(H_2O)_{x-1}(OH)]}{[M(H_2O)_x]}$$
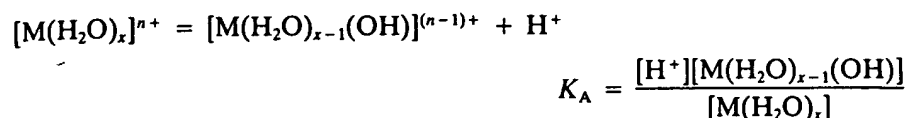
The acidities vary widely, as the following K_A values show:

M in $[M(H_2O)_6]^{n+}$	K_A
Al^{III}	1.12×10^{-5}
Cr^{III}	1.26×10^{-4}
Fe^{III}	6.3×10^{-3}

Coordinated water molecules in other complexes also dissociate in the same way, for example,

$$[Co(NH_3)_5(H_2O)]^{3+} = [Co(NH_3)_5(OH)]^{2+} + H^+ \qquad K \approx 10^{-5.7}$$
$$[Pt(NH_3)_4(H_2O)_2]^{4+} = [Pt(NH_3)_4(H_2O)(OH)]^{3+} + H^+ \qquad K \approx 10^{-2}$$
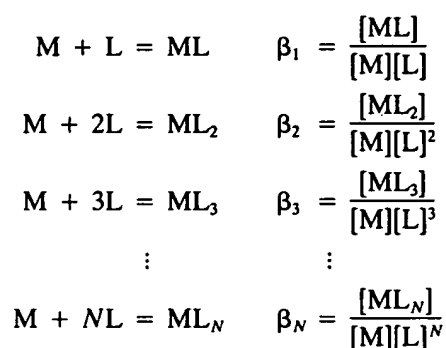
2-3. Formation Constants of Complexes

The thermodynamic stability of a complex can be indicated by an equilibrium constant relating its concentration to the concentration of other species *when the system has reached equilibrium*. The kinetic stability of a species refers to the speed with which transformations leading to the attainment of equilibrium will occur. This section considers problems of thermodynamic stability, that is, the nature of equilibria once they are established.

If in a solution containing aquated metal ions M and unidentate ligands L, only soluble mononuclear complexes are formed, the system at equilibrium may be described by the following equations and equilibrium constants:

$$M + L = ML \qquad K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L = ML_2 \qquad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_2 + L = ML_3 \qquad K_3 = \frac{[ML_3]}{[ML_2][L]}$$

$$\vdots \qquad\qquad \vdots$$

$$ML_{N-1} + L = ML_N \qquad K_N = \frac{[ML_N]}{[ML_{N-1}][L]}$$
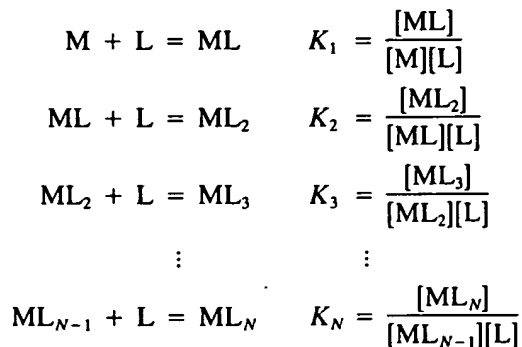
There will be N such equilibria, where N represents the maximum coordination number of the metal ion M for the ligand L, and N may vary from one ligand to another. For instance, Al^{3+} forms $AlCl_4^-$ and AlF_6^{3-} and Co^{2+} forms $CoCl_4^{2-}$ and $Co(NH_3)_6^{2+}$, as the highest complexes with the ligands indicated.

Another way of expressing the equilibrium relations follows:

$$M + L = ML \qquad \beta_1 = \frac{[ML]}{[M][L]}$$

$$M + 2L = ML_2 \qquad \beta_2 = \frac{[ML_2]}{[M][L]^2}$$

$$M + 3L = ML_3 \qquad \beta_3 = \frac{[ML_3]}{[M][L]^3}$$

$$\vdots \qquad\qquad \vdots$$

$$M + NL = ML_N \qquad \beta_N = \frac{[ML_N]}{[M][L]^N}$$

Since there can be only N independent equilibria in such a system, it is clear that the K_i's and the β_i's must be related. The relationship is indeed rather obvious. Consider, for example, the expression for β_3. Let us multiply both numerator and denominator by $[ML][ML_2]$ and then rearrange slightly:

$$\beta_3 = \frac{[ML_3]}{[M][L]^3} \cdot \frac{[ML][ML_2]}{[ML][ML_2]}$$

$$= \frac{[ML]}{[M][L]} \cdot \frac{[ML_2]}{[ML][L]} \cdot \frac{[ML_3]}{[ML_2][L]}$$

It is not difficult to see that this kind of relationship is perfectly general, namely,

$$\beta_k = K_1 K_2 K_3 \cdots K_k = \prod_{i=1}^{i=k} K_i$$

The K_i's are called the *stepwise formation constants* (or stepwise stability constants), and the β_i's are called the *overall formation constants* (or overall stability constants); each type has its special convenience in certain cases.

In all of the previous equilibria we have written the metal ion without specifying charge or degree of solvation. The former omission is obviously of no importance, for the equilibria may be expressed as above whatever the charges. Omission of the water molecules is a convention that is usually convenient and harmless. It must be remembered when necessary. See, for example, the discussion of the chelate effect, in the next section.

With only a few exceptions, there is generally a slowly descending progression in the values of the K_i's in any particular system. This is illustrated

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$$\beta_1 = \frac{[ML]}{[M][L]}$$

$$\beta_2 = \frac{[ML_2]}{[M][L]^2}$$

$$\beta_3 = \frac{[ML_3]}{[M][L]^3}$$

$$\vdots$$

$$\beta_N = \frac{[ML_N]}{[M][L]^N}$$

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and then rearrange slightly:

$$\frac{[L_2]}{[L_2]}$$

$$\cdot \frac{[ML_3]}{[ML_2][L]}$$

elationship is perfectly general,

$$= \prod_{i=1}^{i=k} K_i$$

$\imath$ constants (or stepwise stability
l formation constants (or overall
convenience in certain cases.
: written the metal ion without
ie former omission is obviously
:xpressed as above whatever the
is a convention that is usually
·bered when necessary. See, for
, in the next section.

erally a slowly descending pro-
icular system. This is illustrated

by the data for the Cd^{II}–NH_3 system where the ligands are uncharged and by
the Cd^{II}–CN^- system where the ligands are charged.

$$Cd^{2+} + NH_3 = [Cd(NH_3)]^{2+} \qquad K = 10^{2.65}$$

$$[Cd(NH_3)]^{2+} + NH_3 = [Cd(NH_3)_2]^{2+} \qquad K = 10^{2.10}$$

$$[Cd(NH_3)_2]^{2+} + NH_3 = [Cd(NH_3)_3]^{2+} \qquad K = 10^{1.44}$$

$$[Cd(NH_3)_3]^{2+} + NH_3 = [Cd(NH_3)_4]^{2+} \qquad K = 10^{0.93} \qquad (\beta_4 = 10^{7.12})$$

$$Cd^{2+} + CN^- = [Cd(CN)]^+ \qquad K = 10^{5.48}$$

$$[Cd(CN)]^+ + CN^- = [Cd(CN)_2] \qquad K = 10^{5.12}$$

$$[Cd(CN)_2] + CN^- = [Cd(CN)_3]^- \qquad K = 10^{4.63}$$

$$[Cd(CN)_3]^- + CN^- = [Cd(CN)_4]^{2-} \qquad K = 10^{3.65} \qquad (\beta_4 = 10^{18.8})$$
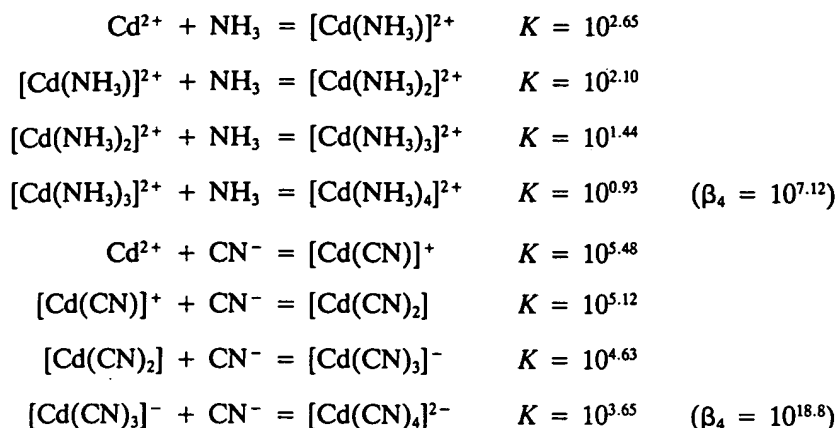
Thus, typically, as ligand is added to the solution of metal ion, ML is first
formed more rapidly than any other complex in the series. As addition of
ligand is continued, the ML_2 concentration rises rapidly, while the ML con-
centration drops, then ML_3 becomes dominant, ML and ML_2 becoming un-
important, and so forth, until the highest complex ML_N is formed, to the
nearly complete exclusion of all others at very high ligand concentrations.
These relationships are conveniently displayed in diagrams such as those
shown in Fig. 2-1.

A steady decrease in K_i values with increasing i is to be expected, provided
there are only slight changes in the metal-ligand bond energies as a function
of i, which is usually the case. For example, in the Ni^{2+}–NH_3 system to be
discussed next, the enthalpies of the successive reactions $Ni(NH_3)_{i-1} + NH_3 =$
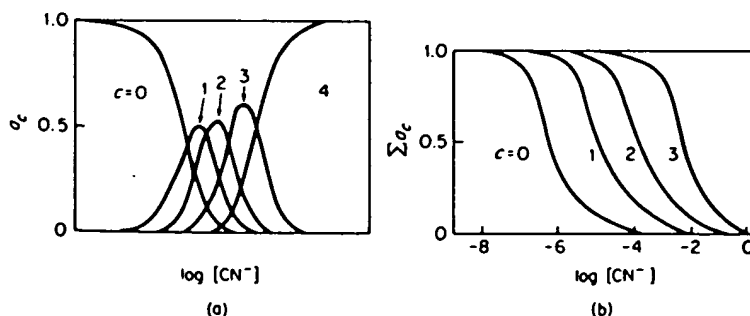$Ni(NH_3)_i$ are all within the range 16.7 to 18.0 kJ mol^{-1}.

FIG. 2-1. Plots of the proportions of the various complexes $[Cd(CN)_c]^{(2-c)+}$ as a function of the
ligand concentration.

$$\alpha_c = [Cd(CN)_c]/\text{total Cd} \qquad \Sigma\alpha_c = \sum_{c=0}^{4} [Cd(CN)_c]/\text{total Cd}$$

[Reproduced by permission from F. J. C. Rossetti, in *Modern Coordination Chemistry*, J. Lewis
and R. G. Wilkins, Eds., Interscience, 1960, p. 10.

There are several reasons for a steady decrease in K_i values as the number of ligands increases: (1) statistical factors, (2) increased steric hindrance as the number of ligands increases if they are bulkier than the H_2O molecules they replace, (3) Coulombic factors, mainly in complexes with charged ligands. The statistical factors may be treated in the following way.[2] Suppose, as is almost certainly the case for Ni^{2+}, that the coordination number remains the same throughout the series $[M(H_2O)_N] \cdots [M(H_2O)_{N-n}L_n] \cdots [ML_N]$. The $[M(H_2O)_{N-n}L_n]$ species has n sites from which to lose a ligand, whereas the species $[M(H_2O)_{N-n+1}L_{n-1}]$ has $(N - n + 1)$ sites at which to gain a ligand. Thus the relative probability of passing from $[M(H_2O)_{N-n+1}L_{n-1}]$ to $[M(H_2O)_{N-n}L_n]$ is proportional to $(N - n + 1)/n$. Similarly, the relative probability of passing from $[M(H_2O)_{N-n}L_n]$ to $[M(H_2O)_{N-n-1}L_{n+1}]$ is proportional to $(N - n)/(n + 1)$. Hence on the basis of these statistical considerations alone, we expect

$$K_{n+1}/K_n = \frac{N - n}{n + 1} \div \frac{N - n + 1}{n} = \frac{n(N - n)}{(n + 1)(N - n + 1)}$$

In the Ni^{2+}–NH_3 system ($N = 6$), we find the comparison between experimental ratios of successive constants and those calculated from the previous formula to be as shown in Table 2-2. The experimental ratios are consistently smaller than the statistically expected ones, which is typical and shows that other factors are also of importance.

There are cases where the experimental ratios of the constants do not remain constant or change monotonically; instead, one of them is singularly large or small. There are several reasons for this: (1) an abrupt change in coordination number and hybridization at some stage of the sequence of complexes, (2) special steric effects that become operative only at a certain stage of coordination, and (3) an abrupt change in electronic structure of the metal ion at a certain stage of complexation. Each of these is now illustrated.

Values of K_3/K_2 are anomalously low for the halogeno complexes of mercury (II); HgX_2 species are linear, whereas $[HgX_4]^{2+}$ species are tetrahedral. Presumably the change from sp to sp^3 hybridization occurs on going from

TABLE 2-2
Comparison of Experimental and Statistical Formation
Constants of Ni^{2+}–NH_3 Complexes

	Experimental	Statistical
K_2/K_1	0.28	0.417
K_3/K_2	0.31	0.533
K_4/K_3	0.29	0.562
K_5/K_4	0.36	0.533
K_6/K_5	0.2	0.417

[2]For a more elaborate discussion see R. Pizer, *Inorg. Chem.*, 1984, **23**, 3027.

ease in K_i values as the number
) increased steric hindrance as
ulkier than the H_2O molecules
in complexes with charged lig-
1 the following way.[2] Suppose,
e coordination number remains
$[M(H_2O)_{N-n}L_n] \cdots [ML_N]$. The
h to lose a ligand, whereas the
sites at which to gain a ligand.
from $[M(H_2O)_{N-n+1}L_{n-1}]$ to
$- 1)/n$. Similarly, the relative
to $[M(H_2O)_{N-n-1}L_{n+1}]$ is pro-
e basis of these statistical con-

$$\frac{n(N - n)}{(n + 1)(N - n + 1)}$$

l the comparison between ex-
those calculated from the pre-
e experimental ratios are con-
ones, which is typical and shows

atios of the constants do not
ead, one of them is singularly
this: (1) an abrupt change in
ime stage of the sequence of
ne operative only at a certain
e in electronic structure of the
ach of these is now illustrated.
e halogeno complexes of mer-
$gX_4]^{2+}$ species are tetrahedral.
lization occurs on going from

tistical Formation
nplexes

	Statistical
	0.417
	0.533
	0.562
	0.533
	0.417

m., 1984, **23**, 3027.

HgX_2 to $[HgX_3]^-$. K_3/K_2 is anomalously small for the ethylenediamine complexes of Zn^{II}, and this is believed to be due to the change from tetrahedral to octahedral coordination if it is assumed that $[Zn\ en_2]^{2+}$ is tetrahedral. For the Ag^+–NH_3 system $K_2 > K_1$, indicating that the linear structure is probably attained with $[Ag(NH_3)_2]^+$ but not with $[Ag(NH_3)(H_2O)_{3(or\ 5)}]^+$.

With 6,6'-dimethyl-2,2'-bipyridine (2-IX), many metal ions that form tris-2,2'-bipyridine complexes form only bis or mono complexes, or, in some cases, no isolable complexes at all, because of the steric hindrance between the methyl groups and other ligands attached to the ion.

(2-IX)
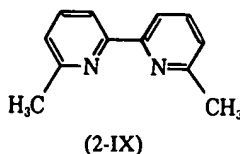
In the series of complexes of Fe^{II} with 1,10-phenanthroline (and also with 2,2'-bipyridine), K_3 is greater than K_2. This is because the tris complex is diamagnetic (i.e., the Fe^{2+} ion has the low-spin state t_{2g}^6) whereas in the mono and bis complexes, as in the aqua ion, there are four unpaired electrons. This change from the $t_{2g}^4e_g^2$ to the t_{2g}^6 causes the enthalpy change for addition of the third ligand to be anomalously large because the e_g electrons are antibonding.

2-4. The Chelate and Macrocyclic Effects[3]

The term "chelate effect" refers to the enhanced stability of a complex system containing chelate rings as compared to the stability of a system that is as similar as possible but contains none or fewer rings. As an example, consider the following equilibrium constants:

$$Ni^{2+}(aq) + 6NH_3(aq) = [Ni(NH_3)_6]^{2+}(aq) \qquad \log \beta = 8.61$$
$$Ni^{2+}(aq) + 3en(aq) = [Ni\ en_3]^{2+}(aq) \qquad \log \beta = 18.28$$
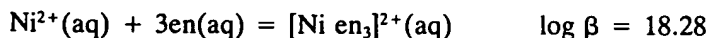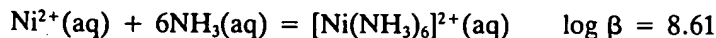
The system $[Ni\ en_3]^{2+}$ in which three chelate rings are formed is nearly 10^{10} times as stable as that in which no such ring is formed. Although the effect is not always so pronounced, such a chelate effect is a very general one.

To understand this effect, we must invoke the thermodynamic relationships:

$$\Delta G° = -RT \ln \beta$$
$$\Delta G° = \Delta H° - T\Delta S°$$

Thus β increases as $\Delta G°$ becomes more negative. A more negative $\Delta G°$ can result from making $\Delta H°$ more negative or from making $\Delta S°$ more positive.

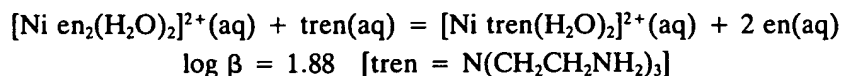[3] J. J. R. Frausto da Silva, *J. Chem. Educ.*, 1983, **60**, 390.

As a very simple case, consider the reactions, and the pertinent thermodynamic data for them, given in Table 2-3. In this case the enthalpy difference is well within experimental error; the chelate effect can thus be traced entirely to the entropy difference.

In the example first cited, the enthalpies make a slight favorable contribution, but the main source of the chelate effect is still to be found in the entropies. We may look at this case in terms of the following metathesis:

$$[Ni(NH_3)_6]^{2+}(aq) + 3 \text{ en}(aq)$$
$$= [Ni \text{ en}_3]^{2+}(aq) + 6NH_3(aq) \qquad \log \beta = 9.67$$
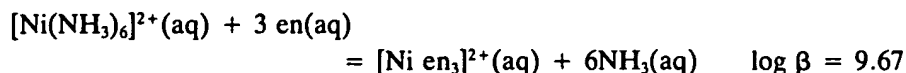
for which the enthalpy change is $-12.1 \text{ kJ mol}^{-1}$, whereas $-T\Delta S° = -43.0$ kJ mol^{-1}. The enthalpy change corresponds very closely to that expected from the increased crystal field stabilization energy of $[Ni \text{ en}_3]^{2+}$, which is estimated from spectral data to be $-11.5 \text{ kJ mol}^{-1}$ and can presumably be so explained.

As a final example, which illustrates the existence of a chelate effect despite an unfavorable enthalpy term, we may use the reaction

$$[Ni \text{ en}_2(H_2O)_2]^{2+}(aq) + \text{tren}(aq) = [Ni \text{ tren}(H_2O)_2]^{2+}(aq) + 2 \text{ en}(aq)$$
$$\log \beta = 1.88 \quad [\text{tren} = N(CH_2CH_2NH_2)_3]$$

For this reaction we have $\Delta H° = +13.0$, $-T\Delta S° = -23.7$, and $\Delta G° = -10.7$ (all in kJ mol^{-1}). The positive enthalpy change can be attributed both to greater steric strain resulting from the presence of three fused chelate rings in Ni tren, and to the inherently weaker M—N bond when N is a tertiary rather than a primary nitrogen atom. Nevertheless, the greater number of chelate rings (3 vs. 2) leads to greater stability, owing to an entropy effect that is only partially canceled by the unfavorable enthalpy change.

Probably the main cause of the large entropy increase in each of the three cases we have been considering is the net increase in the number of unbound molecules—ligands *per se* or water molecules. Thus although 6 NH_3 displace 6 H_2O, making no net change in the number of independent molecules, it takes only 3 en molecules to displace 6 H_2O. Another more pictorial way to look at the problem is to visualize a chelate ligand with one end attached to the metal ion.[4] The other end cannot then get very far away, and the prob-

TABLE 2-3
Two Reactions Illustrating a Purely Entropy-Based Chelate Effect

Cd²⁺(aq) + 4CH₃NH₂(aq) = [Cd(NH₂CH₃)₄]²⁺(aq)			log β = 6.52	

$Cd^{2+}(aq) + 4CH_3NH_2(aq) = [Cd(NH_2CH_3)_4]^{2+}(aq) \qquad \log \beta = 6.52$
$Cd^{2+}(aq) + 2H_2NCH_2CH_2NH_2(aq) = [Cd(en)_2]^{2+}(aq) \qquad \log \beta = 10.6$

Ligands	$\Delta H°$ (kJ mol⁻¹)	$\Delta S°$ (J mol⁻¹ deg⁻¹)	$-T\Delta S°$ (kJ mol⁻¹)	$\Delta G°$ (kJ mol⁻¹)
4CH₃NH₂	−57.3	−67.3	20.1	−37.2
2 en	−56.5	+14.1	−4.2	−60.7

[4]D. R. Rosseinsky, *J. Chem. Soc. Dalton Trans.*, 1979, 732.

ctions, and the pertinent thermo-
in this case the enthalpy difference
e effect can thus be traced entirely

:s make a slight favorable contri-
: effect is still to be found in the
ns of the following metathesis:

:q) + 6NH₃(aq)   log β = 9.67

mol⁻¹, whereas −$T\Delta S°$ = −43.0
very closely to that expected from
зy of [Ni en₃]²⁺, which is estimated
1 can presumably be so explained.
·xistence of a chelate effect despite
the reaction

tren(H₂O)₂]²⁺(aq) + 2 en(aq)
(CH₂CH₂NH₂)₃]

, −$T\Delta S°$ = −23.7, and $\Delta G°$ =
lpy change can be attributed both
:sence of three fused chelate rings
M—N bond when N is a tertiary
ertheless, the greater number of
зility, owing to an entropy effect
orable enthalpy change.
ropy increase in each of the three
:crease in the number of unbound
es. Thus although 6 NH₃ displace
ber of independent molecules, it
). Another more pictorial way to
: ligand with one end attached to
get very far away, and the prob-

tropy-Based Chelate Effect

ZH₃)₄]²⁺(aq)	log β = 6.52	
i(en)₂]²⁺(aq)	log β = 10.6	

−$T\Delta S°$ (kJ mol⁻¹)	$\Delta G°$ (kJ mol⁻¹)
20.1	−37.2
−4.2	−60.7

9, 732.

---

ability of it, too, becoming attached to the metal atom is greater than if this other end were instead another independent molecule, which would have access to a much larger volume of the solution.

The latter view provides an explanation for the decreasing magnitude of the chelate effect with increasing ring size, as illustrated by data such as those shown below for copper complexes of H₂N(CH₂)₂NH₂ and H₂N(CH₂)₃NH₂(tn):

· [Cu en₂]²⁺(aq) + 2tn(aq) = [Cu tn₂]²⁺(aq) + 2 en(aq)   log β = −2.86
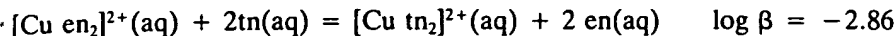
Of course, when the ring that must be formed becomes sufficiently large (seven membered or more), it becomes more probable that the other end of the chelate molecule will contact another metal ion than that it will come around to the first one and complete the ring. Table 2-4 summarizes the factors influencing the stabilities of complexes.

The Macrocyclic Effect. This term refers to the greater thermodynamic stability of a complex with a cyclic polydentate ligand when compared to the complex formed by a comparable noncyclic ligand. A representative comparison would be between the following pair:
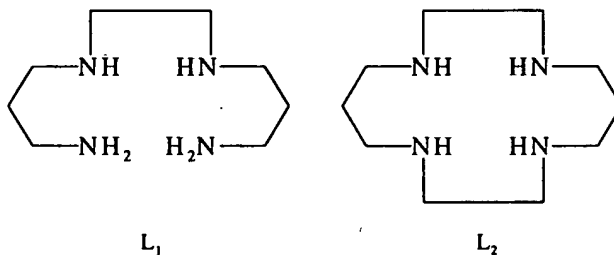
L₁   L₂

The formation of zinc (II) complexes by these two ligands, that is, the reactions (2-1) have been shown[5] to have the following thermodynamic

$$Zn^{2+}(aq) + L_i(aq) \longrightarrow ZnL_i^{2+}(aq) \qquad (2\text{-}1)$$

parameters:

	L₁	L₂
log K	11.25	15.34
−$\Delta H°$ (kJ mol⁻¹)	44.4	61.9
$\Delta S°$ (J deg⁻¹ mol⁻¹)	66.5	85.8

The gross macrocyclic effect is evident in the increase of 4.09 units in log K. It can be seen that the overall effect is of both enthalpic and entropic origin. The relative importance of these two contributions varies from case

[5] M. Micheloni and P. Paoletti, *Inorg. Chim, Acta*, 1980, **43**, 109.

TABLE 2-4
Factors Influencing Solution Stability of Complexes[a]

Enthalpy effects	Entropy effects
Variation of bond strength with electronegativities of metal ions and ligand donor atoms	Number of chelate rings Size of chelate ring
Ligand field effects	Changes of solvation on complex formation
Steric and electrostatic repulsion between ligands in complex	Arrangement of chelate rings
Enthalpy effects related to conformation of uncoordinated ligand	Entropy variations in uncoordinated ligands
Other Coulombic forces involving chelate ring formation	Effects resulting from differences in configurational entropies of the ligand in complex compound
Enthalpy of solution of ligands	Entropy of solution of ligands
Change in bond strength when ligand is charged (same donor and acceptor atom)	Entropy of solution of coordinated metal ions

[a]From R. T. Meyers, *Inorg. Chem.*, 1978, **17**, 952.

to case (see ref. 5 for a selection of comparisons), with enthalpy more often providing the dominant contribution.

Cryptate ligands afford a similar enhancement of stability in some cases, but the availability of many ligand conformations makes this a much more complicated situation.[6] Some cryptate selectivity effects for alkali and alkaline earth metal ions are mentioned in Chapters 4 and 5.

TYPES AND CLASSIFICATION OF LIGANDS

2-5. Multi- or Polydentate Ligands

Regardless of whether π-bonding is involved, ligands can have various dentities, and we now illustrate some of the more important types.

Bidentate Ligands. These are very common and can be classified according to the size of the chelate ring formed as in the following examples:

Three-membered
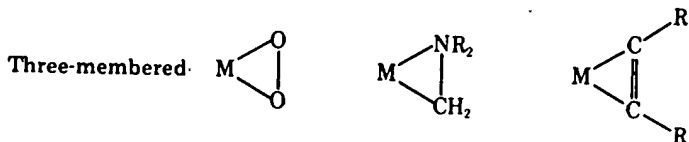
[6]H.-J. Buschmann, *Inorg. Chim. Acta*, 1985, **98**, 43; 1985, **102**, 95.

PLES

·ty of Complexes*

Entropy effects
ımber of chelate rings
ze of chelate ring
ıanges of solvation on complex formation
rrangement of chelate rings
ıtropy variations in uncoordinated ligands
fects resulting from differences in configurational entropies of the ligand in complex compound
ıtropy of solution of ligands
ıtropy of solution of coordinated metal ions

ons), with enthalpy more often

nent of stability in some cases,
ıtions makes this a much more
ity effects for alkali and alkaline
I and 5.

ΙΝ OF LIGANDS

, ligands can have various den-
ıre important types.
mon and can be classified ac-
I as in the following examples:

5, 102, 95.

Four-membered

Five-membered

Six-membered
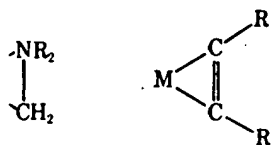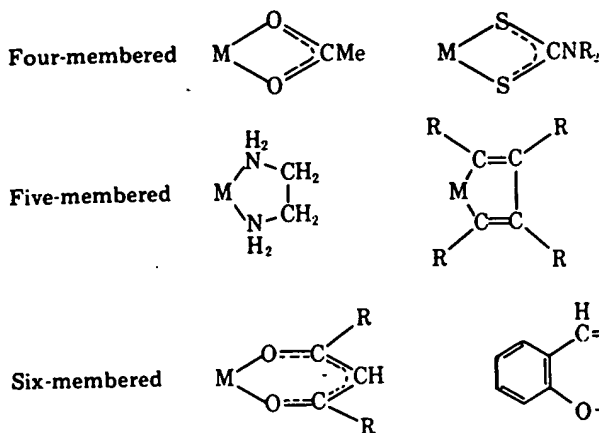
Tridentate Ligands. Some are *obligate planar* such as

Terpyridine (terpy)
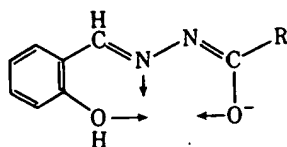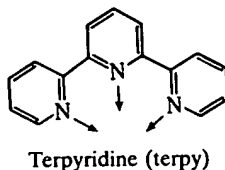
Acylhydrazones of salicylaldehyde

and many similar ones where maintenance of the π conjugation markedly favors planarity. Such ligands must form complexes of the types (2-X) or (2-XI).

(2-X)

(2-XI)
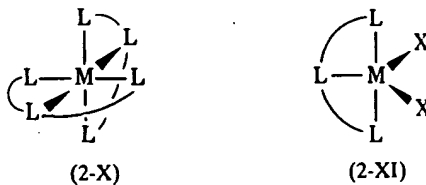
There are also many flexible tridentate ligands such as

$$HN \begin{cases} CH_2CH_2NH_2 \\ CH_2CH_2NH_2 \end{cases}$$

Diethylenetriamine (dien)

$$CH_3As \left\langle \begin{array}{l} (CH_2)_3 \cdot As(CH_3)_2 \\ (CH_2)_3 \cdot As(CH_3)_2 \end{array} \right.$$
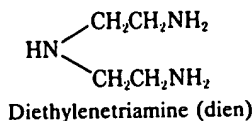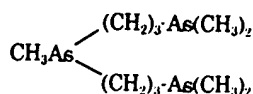
Bis(3-dimethylarsinylpropyl)methylarsine (triars)

which are about equally capable of meridional (2-X and 2-XI) and facial (2-XII) coordination.
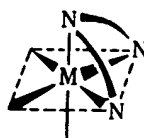
(2-XII)

Quadridentate Ligands. There are four main types:
Open-Chain, Unbranched

$$H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$$
Triethylenetetramine (trien)
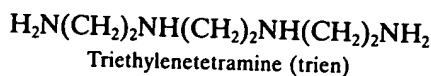
Schiff bases derived from acetylacetone, for example,
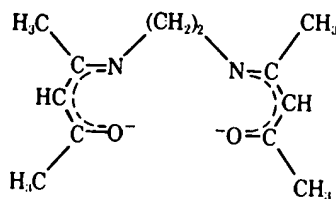
Tripod Ligands. These are of the type X(—Y)$_3$, where X is nitrogen, phosphorus, or arsenic, the Y groups are R$_2$N, R$_2$P, R$_2$As, RS, or RSe, and the connecting chains (—) are (CH$_2$)$_2$, (CH$_2$)$_3$, or *o*-phenylene. Some common ones are

N(CH$_2$CH$_2$NH$_2$)$_3$	tren
N[CH$_2$CH$_2$N(CH$_3$)$_2$]$_3$	Me$_6$tren
N[CH$_2$CH$_2$P(C$_6$H$_5$)$_2$]$_3$	*np*$_3$
P[*o*-C$_6$H$_4$P(C$_6$H$_5$)$_2$]$_3$	QP
N(CH$_2$CH$_2$SCH$_3$)$_3$	TSN
As[*o*-C$_6$H$_4$As(C$_6$H$_5$)$_2$]$_3$	QAS
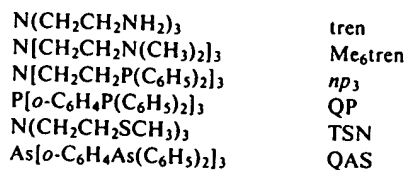
The tripod ligands are used particularly to favor formation of trigonal-bipyramidal complexes of divalent metal ions, as shown schematically in (2-XIII), but they do not invariably give this result. For instance, whereas Ni(*np*$_3$)I$_2$ is trigonal-bipyramidal, Co(*np*$_3$)I$_2$ is square pyramidal (2-XIV).
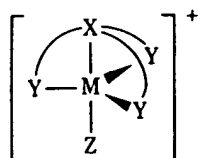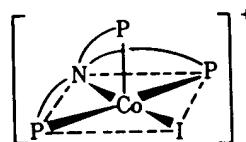
(2-XIII)   (2-XIV)

Macrocyclic. These may be (*a*) planar with unsaturated rings as in porphyrin (2-XV) and its derivatives, although, as discussed later in more detail (Section 10-12) the metal atom may be out of the plane of the nitrogen donor atoms, or (*b*) puckered with saturated rings as in the macrocycles (2-XVI) and (2-XVII).
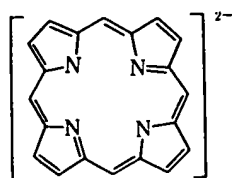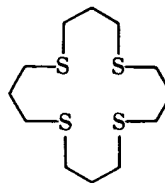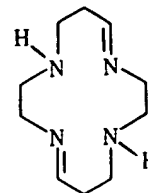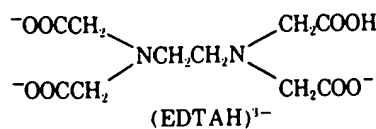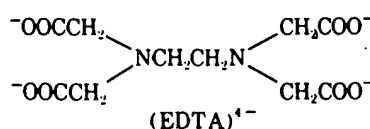

(2-XV)   (2-XVI)   (2-XVII)

Pentadentate and Higher-Dentate Ligands. Perhaps the best known hexadentate ligand is ethylenediaminetetraacetate (EDTA^{4-}), which can also be pentadentate as EDTAH^{3-}.

(EDTA)$^{4-}$ (EDTAH)$^{3-}$

Other important multidentate ligands are the *crown ethers and cryptates.* These are cyclic and polycyclic ligands that form their most important complexes with alkali and alkaline earth ions. The macrocyclic polyethers, commonly called *crown ethers,* are typified by (2-XVIII) and (2-XIX). Since the systematic names for such ligands are very unwieldy, a special nomenclature is used, in which (2-XVIII) and (2-XIX) are called, respectively, 15-crown-5 or 15-C-5 and dibenzo-18-crown-6. These examples should serve to show the rules for the simple nomenclature. Crown ethers with as many as 10 oxygens are known and several [e.g., (2-XIX)] are commercially available.
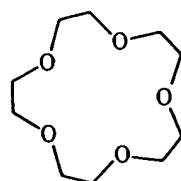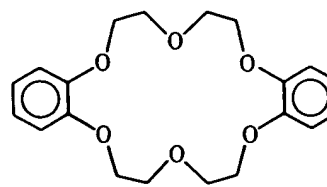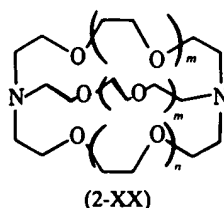

(2-XVIII)   (2-XIX)

The cryptates are bicyclic species, most of which have the general formula (2-XX). Again a simplified code for naming them is a practical necessity. They are called "cryptate-*mmn*," where *m* and *n* are as defined in (2-XX). One of the commonest is cryptate-222.

(2-XX)

These ligands have two characteristics that make them unusually interesting. Because they are chelating ligands of high denticity they give very high formation constants, and since the size of ion that will best fit the cavities can be predetermined by changing the ring size, these ligands can be designed to be selective.

In addition to the cryptates, which are synthesized apart from metal ions and then used to form complexes, there are other types of multicyclic ligand called *encapsulating ligands*, which are synthesized around the metal ion and cannot release it. Two of these are (2-XXI) and (2-XXII). An encapsulation complex allows studies to be carried out under extremely acidic or basic conditions since the metal ion, though it cannot be removed, can be oxidized or reduced. Such ligands also can enforce unusual coordination geometries; in the examples shown the coordination is much closer to trigonal prismatic than to octahedral.

(2-XXI)   (2-XXII)
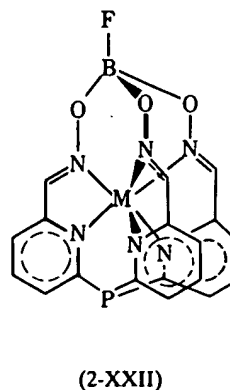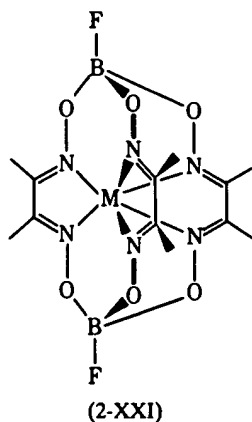
Ligands of Unusual Reach.   Ordinarily bidentate ligands occupy cis positions around a metal ion. This is because two potential donor atoms separated by a chain long enough to be able to span two trans positions would

f which have the general formula

ng them is a practical necessity.

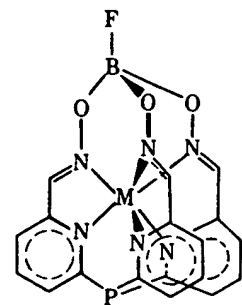and n are as defined in (2-XX).

that make them unusually inter-

of high denticity they give very

 of ion that will best fit the cavi-

ing size, these ligands can be de-

ynthesized apart from metal ions

 other types of multicyclic ligand

hesized around the metal ion and

and (2-XXII). An encapsulation

under extremely acidic or basic

not be removed, can be oxidized

nusual coordination geometries;

much closer to trigonal prismatic

(2-XXII)

bidentate ligands occupy cis po-

two potential donor atoms sepa-

 span two trans positions would

---

have a very low probability of actually doing so. It would be more likely to form only one bond to a given metal atom, while using its second donor atom to coordinate to a different metal atom, or not at all. This is simply an inorganic example of the well-known problem in organic chemistry of synthesizing very large rings. By appropriately designing the connection between the donor atoms, however, ligands that span trans positions in a square complex or the two sites in a linear LML complex can be made. An example is (2-XXIII). Large chelate ring compounds[7] with 12 to 72 membered rings can be made from flexible bidentate ligands [e.g., $Me_2N(CH_2)_nNMe_2$ or $R_2P(CH_2)_nPR_2$].

(2-XXIII)
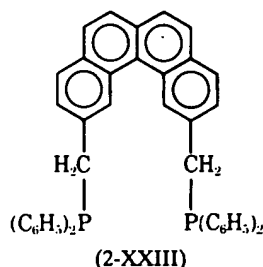
2-6. Conformation of Chelate Rings

Simple diagrams of chelate rings in which the ring conformation is ignored are adequate for many purposes. Indeed, in some cases, such as β-diketonate complexes, the rings are planar and no problem arises. The relative stabilities and certain spectroscopic properties of many chelate complexes, however, can be understood only by considering carefully the effects of the ring conformations, as in the important case of five-membered rings such as those formed by ethylenediamine.

Figure 2-2 shows three ways of viewing the puckered rings, and identifies the absolute configurations in the λ,δ notation. As indicated clearly in the figure, the chelate ring has as its only symmetry element a C_2 axis. It must therefore (see Appendix 5) be chiral, and the two forms of a given ring are enantiomorphs. When this source of enantiomorphism is combined with the two enantiomorphous ways, Λ and Δ of orienting the chelate rings about the metal atom (Fig. 2-3), a number of diastereomeric molecules become possible, specifically, the following eight:

Λ(δδδ)	Δ(λλλ)
Λ(δδλ)	Δ(λλδ)
Λ(δλλ)	Δ(λδδ)
Λ(λλλ)	Δ(δδδ)

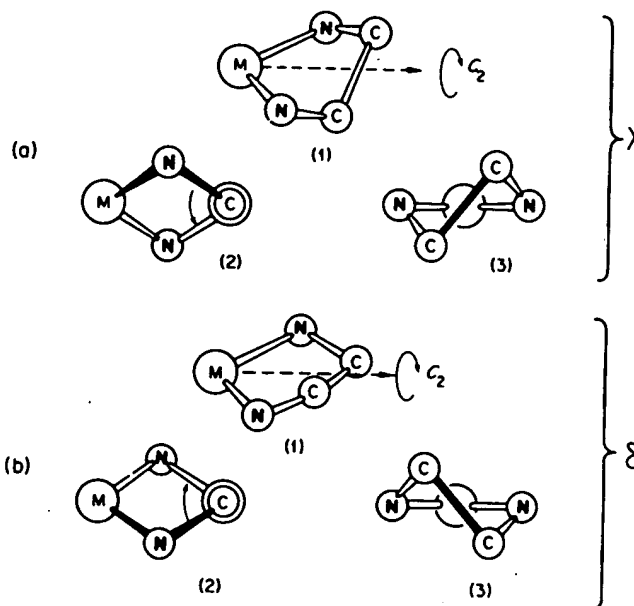[7]L. M. Venanzi *et al.*, *Helv. Chim. Acta*, 1984, **67**, 65.

FIG. 2-2. Different ways of viewing the puckering of ethylenediamine chelate rings. The absolute configurations λ and δ are defined. [Reproduced by permission from C. J. Hawkins; see General References.]

The two columns are here arranged so as to place an enantiomorphous pair on each line. In the following discussion we shall mention only members of the Λ series; analogous energy relationships must of course exist among corresponding members of the Δ series.

The relative stabilities of the four diastereomers have been extensively investigated. First, it can easily be shown that the diastereomers must, in principle, differ in stability because there are different nonbonded (repulsive) interactions between the rings in each case. Figure 2-4 shows these differences for any two rings in the complex. When any reasonable potential function is used to estimate the magnitudes of the repulsive energies, it is concluded that
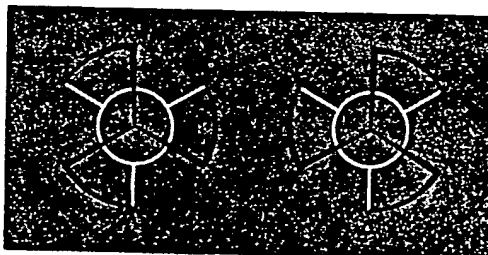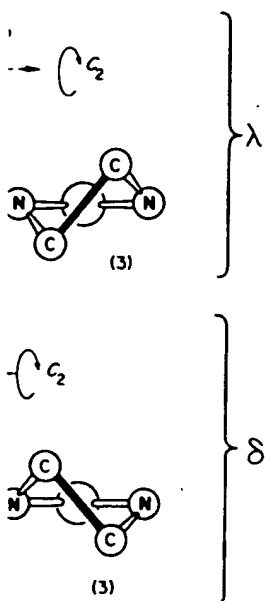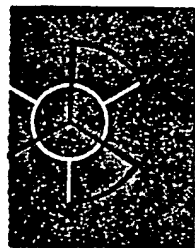

FIG. 2-3. Trischelate octahedral complexes (actual symmetry: D_3) showing how the absolute configurations Λ and Δ are defined according to the translation (twist) of the helices.

(3)

Λ(δδ)

Δ(δδ) ≡ Λ(λλ)

Λ(δλ)

thylenediamine chelate rings. The absolute
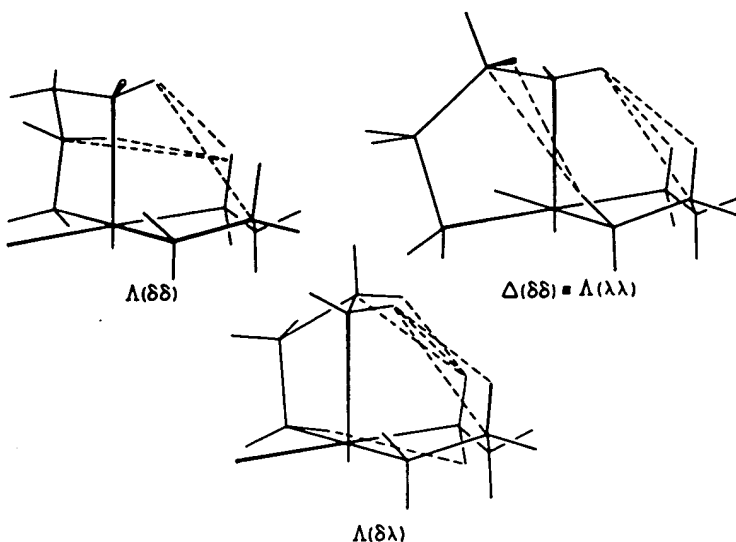:rmission from C. J. Hawkins; see General

FIG. 2-4. The different sets of repulsive interactions that exist between the three different pairs of ring conformations in octahedral ethylenediamine complexes; broken lines represent the significant repulsive interactions. [Reproduced by permission from C. J. Hawkins; see General References.]

to place an enantiomorphous pair
/e shall mention only members of
₁s must of course exist among cor-

tereomers have been extensively
. that the diastereomers must, in
·e different nonbonded (repulsive)
Figure 2-4 shows these differences
₁y reasonable potential function is
₁lsive energies, it is concluded that

the order of decreasing stability is

$$\Lambda(\delta\delta\delta) > \Lambda(\delta\delta\lambda) > \Lambda(\delta\lambda\lambda) > \Lambda(\lambda\lambda\lambda)$$

This is not the actual order, however, because enthalpy differences between diastereomers are rather small (2–3 kJ mol^{-1}), and an entropy factor must also be considered. Entropy favors the δδλ and δλλ species because they are three times as probable as the δδδ and λλλ ones. Hence the best estimate of relative stabilities, which in fact agrees with all experimental data, becomes

$$\Lambda(\delta\delta\lambda) > \Lambda(\delta\delta\delta) \approx \Lambda(\delta\lambda\lambda) \gg \Lambda(\lambda\lambda\lambda)$$

In crystalline compounds, the Δ(δδδ) isomer (or its enantiomorph) has been found most often, but the other three have also been found. These crystallographic results probably prove nothing about the intrinsic relative stabilities, since hydrogen bonding and other intermolecular interactions can easily outweigh the small intrinsic energy differences.

Nuclear magnetic resonance studies of solutions of Ru^{II}, Pt^{IV}, Ni^{II}, Rh^{III}, Ir^{III}, and Co^{III} [M en$_3$]$^{n+}$ complexes have yielded the most useful data, and the general conclusions seem to be that the order of stability suggested here is correct and that ring inversions are very rapid. Both experiment and theory suggest that the barrier to ring inversion is only ~25 kJ mol^{-1}. Thus the four diastereomers of each overall form (Λ or Δ) are in labile equilibrium.

One of the interesting and important applications of the foregoing type of analysis is to the determination of absolute Δ or Λ configurations by using
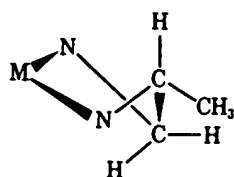

:ymmetry: D₃) showing how the absolute
ranslation (twist) of the helices.

FIG. 2-5. The absolute configuration and expected conformation (i.e., with an equatorial CH_3 group) for an M(l-pn) chelate ring.

substituted ethylenediamine ligands of known absolute configuration. This is nicely illustrated by the $[Co(l\text{-pn})_3]^{3+}$ isomers. The absolute configuration of l-pn [pn = 1,2-diaminopropane, $NH_2CH(CH_3)$—CH_2NH_2] is known. It would also be expected from consideration of repulsions between rings in the tris complex (as indicated in Fig. 2-4) that pn chelate rings would always take a conformation that puts the CH_3 group in an equatorial position. Hence, an l-pn ring can be confidently expected to have the δ conformation shown in Fig. 2-5. Note that because of the extreme unfavorability of having axial CH_3 groups, only two tris complexes are expected to occur, namely, $\Lambda(\delta\delta\delta)$ and $\Delta(\delta\delta\delta)$. But by the arguments already advanced for en rings, the Λ isomer should be the more stable of these two, by 5 to 10 kJ mol^{-1}. Thus we predict that the most stable $[Co(l\text{-pn})_3]^{3+}$ isomer must have the absolute configuration Λ about the metal.

In fact, the most stable $[Co(l\text{-pn})_3]^{3+}$ isomer is the one with + rotation at the sodium-D line, and it has the same circular dichroism spectrum, hence the same absolute configuration as $(+)$-$[Co\,en_3]^{3+}$. The absolute configuration of the latter has been determined, and it is indeed Λ. Thus the argument based on conformational analysis is validated.

2-7. Second Sphere Coordination

The preceding discussion has dealt only with the ligands in direct contact with the metal ion—the *first coordination sphere* (FCS). Undoubtedly the next layer of molecules or ions—the *second coordination sphere* (SCS)—also displays a type of organization different from that in bulk solvent and dictated in part by its proximity to the metal ion and its FCS. In general, however, it is hard to establish any firm picture of the SCS, when it consists simply of a collection of solvent molecules. However, structured second coordination spheres formed by macrocyclic ligands can be often characterized in more detail, even by X-ray crystallography.

In many cases the major links between the two coordination spheres are hydrogen bonds between protic ligands (NH_3, en, and H_2O) in the FCS and the oxygen atoms of macrocyclic ethers that provide the SCS.[8] An example is provided by the "supercomplex" between $(COD)Rh(NH_3)_2$ and dibenzo-24-crown-8. Conversely, there may be hydrogen bonds between a surrounding

[8]H. M. Colquhoun *et al.*, *J. Chem. Soc. Dalton Trans.*, **1986**, 1939; *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 487 (review).

iguration and expected conformation group) for an M(*l*-pn) chelate ring.

absolute configuration. This is
The absolute configuration of
]—CH$_2$NH$_2$] is known. It would
sions between rings in the tris
late rings would always take a
equatorial position. Hence, an
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avorability of having axial CH$_3$
to occur, namely, Λ(δδδ) and
:ed for en rings, the Λ isomer
) 10 kJ mol^{-1}. Thus we predict
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: is the one with + rotation at
ar dichroism spectrum, hence
]$^{3+}$. The absolute configuration
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e ligands in direct contact with
FCS). Undoubtedly the next
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two coordination spheres are
en, and H$_2$O) in the FCS and
rovide the SCS.[8] An example
COD)Rh(NH$_3$)$_2$ and dibenzo-
bonds between a surrounding

', 1939; *Angew. Chem. Int. Ed. Engl.*,

protonated amine macrocycle and a central anionic complex,[9] as shown schematically in (2-XXIV). In both of these types of "supercomplex" the H-bonding forces are supplemented by other noncovalent interactions, and it would appear that in some cases, as illustrated by the complexes of (COD)PtCl$_2$ and [(COD)RhCl]$_2$ with cyclodextrins,[10] the forces between the FCS and the SCS are entirely of the secondary types, namely, dipole–dipole, dipole–induced dipole, van der Waals, and so on.
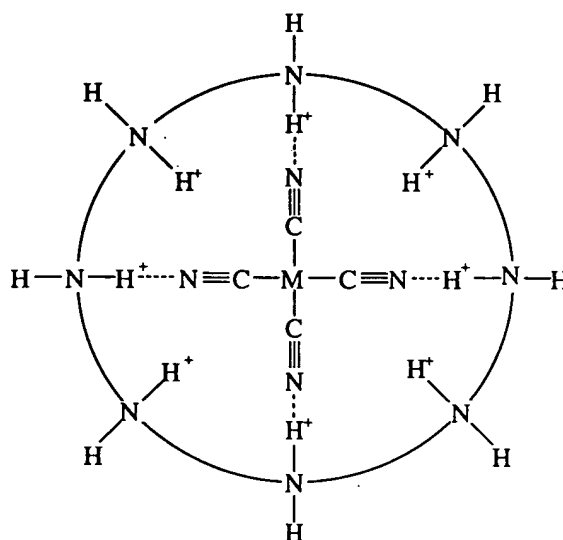
(2-XXIV)

π-ACID OR π-BONDING LIGANDS: π COMPLEXES

The ligands for which π bonding is important are carbon monoxide, isocyanides, substituted phosphines, arsines, stibines or sulfides, nitric oxide, and various molecules with delocalized π orbitals. These include pyridine, 2,2'-bipyridine, 1,10-phenanthroline, and certain ligands containing 1,2-dithioketone or 1,2-dithiolene groups, such as the dithiomaleonitrile anion. Diverse complexes exist, ranging from binary molecular compounds such as Cr(CO)$_6$ or Ni(PF$_3$)$_4$ through mixed species such as Co(CO)$_3$NO and (C$_6$H$_5$)$_3$P Fe(CO)$_4$, to complex ions such as [Fe(CN)$_5$CO]$^{3-}$, [Mo(CO)$_5$I]$^-$, [Mn(CNR)$_6$]$^+$, [V phen$_3$]$^+$, and {Ni[S$_2$C$_2$(CN)$_2$]$_2$}$^{2-}$.

In many of these complexes, the metal atoms are in low-positive, zero, or negative formal oxidation states. It is a characteristic of the ligands that they can stabilize low oxidation states. This property is associated with the fact

[9]V. Balzani *et al.*, *J. Chem. Soc. Chem. Commun.*, **1984**, 55.
[10]A. Harada and S. Takahashi, *J. Chem. Soc. Chem. Commun.*, **1986**, 1229.

that in addition to lone pairs, these ligands possess *vacant π orbitals*. These vacant orbitals accept electron density from filled metal orbitals to form a type of π bonding that supplements the σ bonding arising from lone-pair donation; high electron density on the metal atom—of necessity in low oxidation states—thus can be delocalized onto the ligands. The ability of ligands to accept electron density into low-lying empty π orbitals can be called π *acidity,* the word "acidity" being used in the Lewis sense.

There are many unsaturated organic molecules and ions that are also capable of forming complexes with transition metals in low oxidation states, and these are called π *complexes*. There is a qualitative difference from π-acid ligands. The latter form bonds to the metal involving σ orbitals and π orbitals whose nodal planes include the axis of the σ bond. For the π-complexing ligands such as alkenes, arenes, and allyl groups, *both* the donation and back-acceptance (see next section) of electron density by the ligand are accomplished using ligand π orbitals. The metal is thus out of the molecular plane of the ligand, whereas with π-acid ligands the metal atom lies along the axes of the linear ligands or in the plane of planar ones.

In a third class of ligand that involves π bonding there are metal-oxygen or metal-nitrogen multiple bonds, as in $O{=}VCl_3$, MnO_4^-, and $N{\equiv}OsO_3^-$. Here the electron flow is in the opposite sense to that in the bonding of π-acid ligands (i.e., from p orbitals on O or N to the metal d orbitals).

We now survey the main classes of ligands that form π bonds to metal atoms. The chemical properties of metal carbonyls and metal complexes with the other π-bonding ligands will be presented in Chapter 22 and in sections dealing with the chemistry of NO, phosphorus (III) compounds, and so on.

2-8. π-Acid Ligands: CO as the Prototype

Ligands capable of accepting an appreciable amount of π-electron density, from the metal atoms into empty π or π^* orbitals of their own are referred to as π-acceptor or π-acid ligands. Of these, carbon monoxide is the most important and the most extensively studied. We shall discuss the principal way in which it forms bonds to metals, namely, in a linear M—C—O fashion in detail here. In Chapter 22, the chemistry of metal carbonyls as a class (including the other forms of bonding in which CO engages) will be discussed. In Section 2-9 the way in which some similar ligands (such as RNC, N_2, NO) function as π-acid ligands will be compared with the behavior of CO.

The way in which CO (and many other π-acid ligands similarly) engages in bonding to a metal atom may be stated as follows:

1. Overlap of a filled carbon σ orbital with a σ-type orbital on the metal atom as in Fig. 2-6a. Electron flow C $\rightarrow$ M in such a dative overlap would lead to an unacceptable concentration of electron density on the metal atom when the latter is not a +2 or more highly charged ion. The metal therefore attempts to reduce this charge (Pauling's electroneutrality principle) by push-
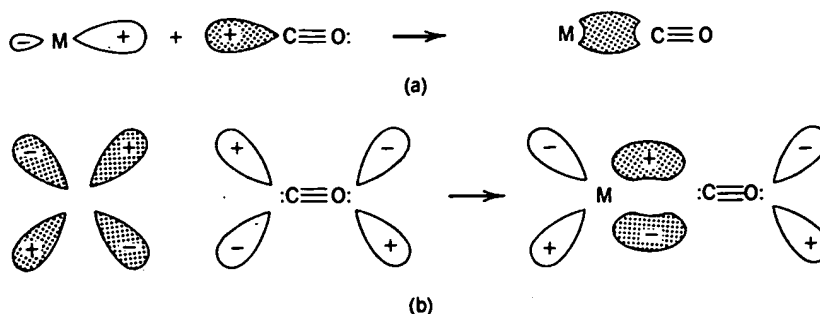
(a)

(b)

FIG. 2-6. (a) The formation of the metal ← carbon σ bond using an unshared pair on the C atom. (b) The formation of the metal → carbon π bond. The other orbitals on the CO are omitted for clarity.

)ossess *vacant π orbitals.* These
filled metal orbitals to form a
bonding arising from lone-pair
atom—of necessity in low oxi-
ie ligands. The ability of ligands
:pty π orbitals can be called π
Lewis sense.

cules and ions that are also ca-
metals in low oxidation states,
: qualitative difference from π-
etal involving σ orbitals and π
of the σ bond. For the π-com-
allyl groups, *both* the donation
ctron density by the ligand are
·tal is thus out of the molecular
ınds the metal atom lies along
of planar ones.

onding there are metal-oxygen
:VCl₃, MnO₄⁻, and N≡OsO₃⁻.
se to that in the bonding of π-
to the metal *d* orbitals).

ls that form π bonds to metal
ınyls and metal complexes with
l in Chapter 22 and in sections
s (III) compounds, and so on.

amount of π-electron density,
ıitals of their own are referred
carbon monoxide is the most
We shall discuss the principal
·, in a linear M—C—O fashion
of metal carbonyls as a class
CO engages) will be discussed.
igands (such as RNC, N₂, NO)
·ith the behavior of CO.
acid ligands similarly) engages
follows:
ı a σ-type orbital on the metal
n such a dative overlap would
ron density on the metal atom
ırged ion. The metal therefore
·oneutrality principle) by push-

ing electrons back to the ligand. This of course is possible *only* if the ligand has suitable acceptor orbitals.

2. A second dative overlap of a filled $d\pi$ or hybrid $dp\pi$ metal orbital with the empty, $p\pi$ orbital on carbon monoxide, which can act as a receptor of electron density (Fig. 2-6b).

This bonding mechanism is *synergic,* since the drift of metal electrons, referred to as "back-bonding", into CO orbitals, will tend to make the CO as a whole negative, hence to increase its basicity via the σ orbital of carbon; at the same time the drift of electrons to the metal in the σ bond tends to make the CO positive, thus enhancing the acceptor strength of the π orbitals. Thus up to a point the effects of σ-bond formation strengthen the π bonding, and vice versa. It may be noted here that dipole moment studies indicate that the moment of an M—C bond is only very low, about 0.5 D, suggesting a close approach to electroneutrality.

There have been many efforts to provide a detailed accounting of the relative importance of σ and π components of the bonding in metal carbonyls by means of molecular orbital calculations.[11] However, even for the simplest molecules, namely, $M(CO)_x$ ($x = 4, 5, 6$), it is not feasible to avoid making some important approximations, whose final effects on the results are uncertain. Hence, it is probably wiser to rely primarily on experimental evidence in attempting to understand the bonding in metal carbonyls and related complexes of π-acid ligands.

Two important and broadly useful lines of physical evidence showing the multiple nature of M—CO bonds are bond lengths and vibrational spectra. According to the preceding description of the bonding, as the extent of back-donation from M to CO increases, the M—C bond becomes stronger and the C≡O bond becomes weaker. Thus, the multiple bonding should be evidenced by shorter M—C and longer C—O bonds as compared to M—C single bonds

[11]C. W. Bauschlicher, Jr., and P. S. Bagus, *J. Chem. Phys.,* 1984, **81**, 5889.

and C≡O triple bonds, respectively. Actually very little information can be obtained from the CO bond lengths, because in the range of bond orders (2–3) concerned, CO bond length is relatively insensitive to bond order. The bond length in CO itself is 1.128 Å, while the bond lengths in metal carbonyl molecules are ~1.15 Å, a shift in the proper direction but of little quantitative significance owing to its small magnitude and the uncertainties (~0.02 Å) in the individual distances. For M—C distances, the sensitivity to bond order in the range concerned (1–2) is relatively high, probably ~0.3 to 0.4 Å per unit of bond order, and good evidence for multiple bonding can therefore be expected from such data. To do this we measure the lengths of M—CO bonds in the same molecule in which some other bond, M—X exists, such that this bond must be single. Then, using the known covalent radius for X, estimating the single bond covalent radius of C to be 0.70 Å when an *sp* hybrid orbital is used (the greater *s* character makes this ~0.07 Å shorter than that for *sp³* carbon), the length for a single M—CO bond *in this molecule* can be estimated and compared with the observed value.

Figure 2-7 shows some substitution products of $Cr(CO)_6$ in which three or four CO groups have been replaced by ligands such as aliphatic amine nitrogen, which has no capacity to compete with CO trans to it for π bonding or PH_3, which has very little capacity to do so. We see that in such cases the remaining CO groups have even shorter Cr—C bonds because of even more extensive development of Cr—C π-back-bonding. The shortening is greater in (b) than in (c), since there is slight π bonding to the phosphorus atoms of PH_3. The shortening is also greater in (d) than in (c) because there are only two CO groups in (d) to compete for the available $d\pi$ electrons of the chromium atom.

From the vibrational spectra of metal carbonyls, it is also possible to infer the existence and extent of M—C multiple bonding. This is most easily done by studying the CO stretching frequencies rather than the MC stretching frequencies, since the former give rise to strong sharp bands, well separated from all other vibrational modes of the molecules. The MC stretching frequencies, on the other hand, are in the same range with other types of vibration (e.g., MCO bends); therefore assignments are not easy to make, nor are the so-called MC stretching modes actually pure MC stretching motions. The inferring of M—C bond orders from the behavior of C—O vibra-
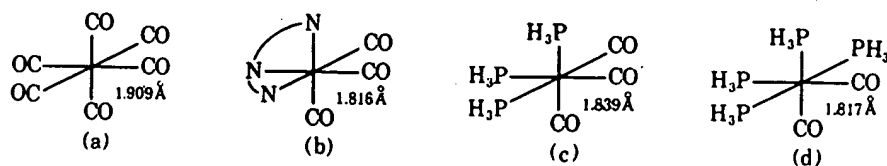

FIG. 2-7. Cr—C bond distances in (a) $Cr(CO)_6$, (b) *fac*-[$H_2N(CH_2)_2NH(CH_2)NH_2$]$Cr(CO)_3$, (c) *fac*-(PH_3)$_3$$Cr(CO)_3$, and (d) *cis*-($PH_3$)$_4$$Cr(CO)_2$. [Data for (b) are from F. A. Cotton and D. C. Richardson, *Inorg. Chem.* 1966, **5**, 1851. Data for (a), (c), and (d) are from G. Huttner and S. Schelle, *J. Crystallogr. Mol. Struct.*, 1971, **1**, 69.]

·y very little information can be
in the range of bond orders (2–
insensitive to bond order. The
bond lengths in metal carbonyl
irection but of little quantitative
: the uncertainties (~0.02 Å) in
s, the sensitivity to bond order
;h, probably ~0.3 to 0.4 Å per
iltiple bonding can therefore be
re the lengths of M—CO bonds
nd, M—X exists, such that this
ovalent radius for X, estimating
70 Å when an *sp* hybrid orbital
).07 Å shorter than that for *sp*³
n this molecule can be estimated

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We see that in such cases the
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(c)   (d)
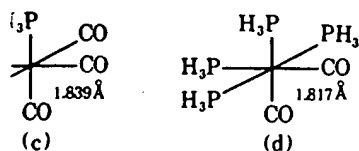
ic-[H₂N(CH₂)₂NH(CH₂)₂NH₂]Cr(CO)₃,
a for (b) are from F. A. Cotton and
(a), (c), and (d) are from G. Huttner

tions depends on the assumption that the valence of C is constant, so that a given increase in the M—C bond order must cause an equal decrease in the C—O bond order; this, in turn, will cause a drop in the CO vibrational frequency.

From the direct comparison of CO stretching frequencies in carbonyl molecules with the stretching frequency of CO itself, certain useful qualitative conclusions can be drawn. The CO molecule has a stretching frequency of 2143 cm⁻¹. Terminal CO groups in neutral metal carbonyl molecules are found in the range 2125 to 1850 cm⁻¹, showing the reduction in CO bond orders. Moreover, when changes are made that should increase the extent of M—C back-bonding, the CO frequencies are shifted to even lower values. Thus if some CO groups are replaced by ligands with low or negligible back-accepting ability, those CO groups that remain must accept *d*π electrons from the metal to a greater extent to prevent the accumulation of negative charge on the metal atom. Thus the frequencies for Cr(CO)₆ are ~2100, 2000, and 1985 cm⁻¹ (exact values vary with phase and solvent) whereas, when three CO's are replaced by amine groups that have essentially no ability to back-accept, as Crdien(CO)₃ (Fig. 2-7b), there are two CO stretching modes with frequencies of ~1900 and 1760 cm⁻¹. Similarly, when we go from Cr(CO)₆ to the isoelectronic V(CO)₆⁻, when more negative charge must be taken from the metal atom, a band is found at ~1860 cm⁻¹ corresponding to the one found at ~2000 cm⁻¹ in Cr(CO)₆. A series of these isoelectronic species illustrating this trend, with their infrared-active CO stretching frequencies (cm⁻¹) is Ni(CO)₄ (~2060); Co(CO)₄⁻ (~1890); Fe(CO)₄²⁻ (~1790). Conversely, a change that would tend to inhibit the shift of electrons from metal to CO π orbitals, such as placing a positive charge on the metal, should cause the CO frequencies to *rise,* and this effect has been observed in several cases, the following being representative:

Mn(CO)₆⁺,~2090   Mndien(CO)₃⁺,~2020,~1900
Cr(CO)₆,~2000   Crdien(CO)₃,~1900,~1760
V(CO)₆⁻, ~1860

To obtain semiquantitative estimates of M—C π bonding from vibrational frequencies, it is first necessary to carry out an approximate dynamical analysis of the CO stretching modes, thus to derive force constants for the CO groups. This procedure is discussed in Section 22-5.

The type of structural and spectroscopic evidence just noted, while persuasive, is nonetheless rather indirect. More direct evidence for M—CO π bonding has recently been obtained by photoelectron spectroscopy.[12] For Cr(CO)₆ and W(CO)₆ the photoionization of one of those electrons that must be responsible for whatever M—CO π bonding exists was carried out and the effect of removing such an electron on the frequency of the totally sym-

[12]J. L. Hubbard and D. L. Lichtenberger, *J. Am. Chem. Soc.,* 1982, **104,** 2132.

metric M—C stretching vibration in the resulting $M(CO)_6^+$ ion measured. The frequency of this vibration was, in each case, found to be significantly lower than that of the corresponding vibration in the neutral $M(CO)_6$ molecule, that is, by 10% for $W(CO)_6^+$ and 15% for $Cr(CO)_6^+$. This unequivocally shows that the orbitals from which the electrons have been removed contribute importantly to the M—C bond strengths. By a further analysis of these same data it was shown that the loss of one such electron causes increases of ~0.14 and 0.10 Å in the Cr—C and W—C distances, respectively.

2-9. Other π-Acid Ligands

We shall specifically mention here the following CO-like π-acid ligands: RNC, N_2, CS, NO, and NS. The first three are isoelectronic with CO, while NO and NS have one more electron. The *chemistry* of compounds that contain these ligands is discussed in later sections (RNC and CS in Chapter 8; N_2, NO, and NS in Chapter 10) and we are concerned here only with discussing their ability to serve as π-acid ligands and how, in each case, it compares with that of CO.

Isocyanide Ligands. (See Section 8-11 for chemistry.) Isocyanides are capable of displaying as great π-acceptor capacity as CO when linked to a metal center capable of strong π donation, and this may be described using the same pattern of orbital overlaps as previously discussed for M—CO bonding. Both spectroscopic evidence (lowering of C—N stretching frequencies) and structural evidence [short M—C distances, such as 1.94 Å in $Cr(CNPh)_6$] demonstrate this. The important difference between CO and RNC is that the latter is not an *obligatory* π acid. That is, while CO is such a weak Lewis base that the stability of M—CO bonds requires the synergic participation of both σ donation and π acceptance, isocyanides are good Lewis bases and can form bonds to higher-valent metal ions where there is essentially only σ donation involved.

It may be noted here that the cyanide ion (CN⁻) is also isoelectronic with CO and RNC, but its capacity to serve as a π acid is much lower and from the point of view of bonding it is perhaps best regarded as a pseudohalide rather than as a π-acid ligand. See Section 8-10 for the chemistry of CN⁻.

Dinitrogen. Although N_2 is isoelectronic with CO and RNC, and isosteric with the former, it is far more inert and the first dinitrogen complex, $[Ru(NH_3)_5(N_2)]^{2+}$ was discovered only in 1965. Dinitrogen can be bound to metal atoms only in the presence of other ligands; there are no homoleptic complexes analogous to those formed by CO or RNC.

The bonding in *linear M—N—N groups* is qualitatively similar to that in terminal M—CO groups; the same two basic components, M ← N_2 σ donation and M → N_2 π acceptance, are involved. The major quantitative differences, which account for the lower stability of N_2 complexes, appear to arise from small differences in the energies of the MO's of CO and N_2. For CO the σ-donor orbital is weakly antibonding, whereas the corresponding orbital for N_2 is of bonding character. Thus N_2 is a significantly poorer σ donor than is

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CO. Now it is observed that in pairs of N$_2$ and CO complexes where the metal and other ligands are identical, the fractional lowerings of N$_2$ and CO frequencies are nearly identical. For the CO complexes, weakening of the CO bond, insofar as electronic factors are concerned, is due entirely to back-donation from metal $d\pi$ orbitals to CO π^* orbitals, with the σ donation slightly canceling some of this effect. For N$_2$ complexes, on the other hand, N≡N bond weakening results from both σ donation and π back-acceptance. The very similar changes in stretching frequencies for these two ligands suggest then that N$_2$ is weaker than CO in both its σ-donor and π-acceptor functions. This in turn would account for the poor stability of N$_2$ complexes in general. Terminal dinitrogen compounds have N—N stretching frequencies in the region 1930 to 2230 cm^{-1} (N$_2$ has $v = 2331$ cm^{-1}). For discussion of chemistry, see Section 10-9.

The CS Ligand.   Although the CS molecule cannot be isolated, complexes containing the M—CS unit are known (cf. Section 8-13). The synergic σ/π interactions in M—CS units are similar to those in M—CO units, but perhaps somewhat stronger.

The NO Ligand.   The NO molecule is closely akin to the CO molecule except that it contains one more electron, which resides in a π^* orbital. Loss of this electron gives NO$^+$ which is isoelectronic with CO.

Just as the CO group reacts with a metal atom that presents an empty σ orbital and a pair of filled $d\pi$ orbitals, as illustrated in Fig. 2-6, to give a linear MCO grouping with a C → M σ bond and a significant degree of M → C π bonding, so the NO group engages in a structurally and electronically analogous reaction with a metal atom that may be considered, at least formally, to present an empty σ orbital and a pair of $d\pi$ orbitals containing only three electrons. The full set of four electrons for the M$d\pi$ → π^*(NO) interactions is thus made up of three electrons from M and one from NO. In effect, NO contributes three electrons to the total bonding configuration under circumstances where CO contributes only two. Thus for purposes of formal electron "bookkeeping," the ligand NO can be regarded as a three-electron donor in the same sense as the ligand CO is considered a two-electron donor. This leads to the following very useful general rules concerning stoichiometry, which may be applied without specifically allocating the difference in the number of electrons to any particular (i.e., σ or π) orbitals:

1. Compounds isoelectronic with one containing an M(CO)$_n$ grouping are those containing M'(CO)$_{n-1}$(NO), M''(CO)$_{n-2}$(NO)$_2$, and so on, where M', M'', and so on, have atomic numbers that are 1, 2, . . . , and so on, <M. Some examples are (η-C$_5$H$_5$)CuCO, (η-C$_5$H$_5$)NiNO; Ni(CO)$_4$, Co(CO)$_3$NO, Fe(CO)$_2$(NO)$_2$, Mn(CO)(NO)$_3$; Fe(CO)$_5$, Mn(CO)$_4$NO.

2. Three CO groups can be replaced by two NO groups. Examples of pairs of compounds so related are
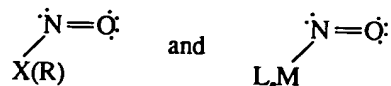
Fe(CO)$_5$	Fe(CO)$_2$(NO)$_2$
Mn(CO)$_4$NO	Mn(CO)(NO)$_3$
Cr(CO)$_6$	Cr(NO)$_4$
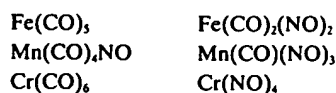
It may be noted that $Cr(NO)_4$ is the only known homoleptic metal nitrosyl complex. It is isoelectronic with $Ni(CO)_4$ and similarly has a tetrahedral structure, with a very short Cr—N distance (1.763 Å).[13] Claims for $Co(NO)_3$, $Fe(NO)_4$, and $Ru(NO)_4$ have never been confirmed.

It should be noted that the designation "linear MNO group" does not disallow a small amount of bending in cases where the group is not in an axially symmetric environment, just as with terminal MCO groups. Thus MNO angles of 161 to 175° may be found in "linear" MNO groups. Truly "bent MNO groups" have angles of 120 to 140°.

In compounds containing both MCO and linear MNO groups, the M—C and M—N bond lengths differ by a fairly constant amount, ~0.07 Å, approximately equal to the expected difference in the C and N radii, and suggest that under comparable circumstances M—CO and M—NO bonds are typically about equally strong. In a chemical sense the M—N bonds appear to be stronger, since substitution reactions on mixed carbonyl nitrosyl compounds typically result in displacement of CO in preference to NO. For example, $Co(CO)_3NO$ reacts with a variety of R_3P, X_3P, amine, and RNC compounds, invariably to yield the $Co(CO)_2(NO)L$ product.

The NO vibration frequencies for linear MNO groups substantiate the idea of extensive M—N π bonding, leading to appreciable population of NO π^* orbitals. Both the NO and O_2^+ species contain one π^* electron and their stretching frequencies are 1860 and 1876 cm⁻, respectively. Thus the observed frequencies in the range 1800–1900 cm⁻¹, which are typical of linear MNO groups in molecules with small or zero charge, indicate the presence of approximately one electron pair shared between metal $d\pi$ and NO π^* orbitals.

Since nitrosyl halides (Section 10-8) and nitroso alkanes are bent, similar metal complexes can be anticipated:

$$\overset{\cdot\cdot}{N}=\overset{\cdot\cdot}{O}: \qquad \text{and} \qquad \overset{\cdot\cdot}{N}=\overset{\cdot\cdot}{O}:$$
$$\diagup \qquad\qquad\qquad \diagup$$
$$X(R) \qquad\qquad\qquad L_nM$$

A typical example is $IrCl_2(NO)(PPh_3)_2$ where the MNO angle is 123°. The NO here is best regarded as a $1e$ donor or as NO⁻; π bonding is not involved. Bridging NO groups, where NO can be regarded as a $3e$ donor, are also known.

These aspects and reactions of coordinated NO are discussed in more detail in Section 10-10.

The sulfur analogues with M—NS bonds are discussed in Section 10-10.

2-10. π-Acid Ligands: Trivalent Phosphorus Compounds

Compounds of the type PX_3 (as well as AsX_3, SbX_3, SX_2, and SeX_2 species), especially when X is relatively electronegative, such as Ph, OR, Cl, or F, are important π-bonding ligands. This is particularly true of PF_3 which forms

[13]K. Hedberg et al., Inorg. Chem., 1985, 24, 2776.
[14]J. F. Nixon, Adv. Inorg. Chem. Radiochem., 1985, 29, 42.

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[15]B. E. Bu
[16]F. W. B.
[17]F. A. Co
[18]W. C. T
1984, 106,
M. Braga,
[19]G. Hun

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:f R₃P, X₃P, amine, and RNC
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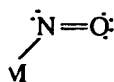
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Compounds

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such as Ph, OR, Cl, or F, are
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many compounds comparable to those of CO,[14] for example, Ni(PF₃)₄ and Cr(PF₃)₆. Tertiary phosphines and phosphites, however, are also much better Lewis bases than CO and can form many complexes where π acidity plays little or no role. This is observed with the phosphine complexes of the early transition metals and with metal atoms of any kind in their higher oxidation states. In compounds such as NbBr₄(PMe₂Ph)₃ or PtCl₄(PMePh₂)₂ the M—P distances show no evidence of significant π bonding. Phosphorus ligands are discussed in Section 11-18.

In almost any CO-containing molecule, one or more CO groups can be replaced by a PX₃ or similar ligand. The ability of PR₃ ligands (R = Me, Et, or Bu) to compete with CO groups for metal dπ electrons can be studied in detail by photoelectron spectroscopy[15] and vibrational spectroscopy in Mo(CO)ₙ(PR₃)₆₋ₙ species and similar ones. The significant σ-donor ability[16] and steric requirements[17] of such ligands is also important in regard to the structures of M(CO)ₓ(PR₃)ᵧ type molecules.

While the occurrence of M → P dative π bonding is a generally acknowledged fact, the explanation for it entails controversy. The classical, and still widely credited, picture is that shown in Fig. 2-8, in which phosphorus specifically employs a pair of its d orbitals to accept metal electrons. However, it has been proposed, on the basis of quantum mechanical calculations that phosphorus p orbitals and the P—X σ* orbitals may play a major role in accepting metal dπ electrons, even to the complete exclusion of the phosphorus dπ orbitals.[18a] Experimental evidence for or against such ideas is lacking. Rotation about the M—P bond with relatively small barriers (32–38 kJ mol⁻¹) can be shown by nmr methods.[18b]
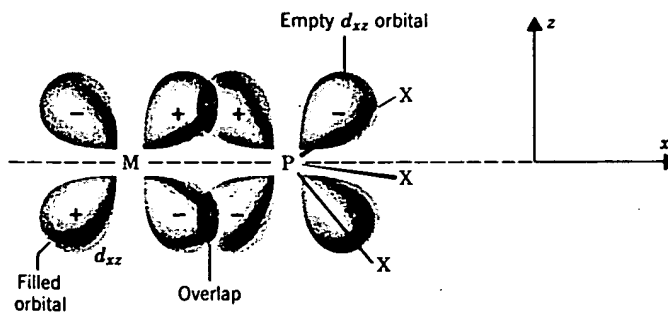

FIG. 2-8. The back-bonding from a filled metal d orbital to an empty phosphorus 3d orbital in the PX₃ ligand taking the internuclear axis as the x axis. An exactly similar overlap occurs in the xy plane using the d_{xy} orbitals.

[15]B. E. Bursten et al., Inorg. Chem., 1984, 23, 4361.
[16]F. W. B. Einstein et al., Inorg. Chem., 1985, 24, 2777.
[17]F. A. Cotton et al., Inorg. Chem., 1982, 21, 294.
[18a]W. C. Trogler et al., J. Am. Chem. Soc., 1983, 105, 7033; D. S. Marynick, J. Am. Chem. Soc., 1984, 106, 4064; A. G. Orpen and N. G. Connelly, J. Chem. Soc. Chem. Commun., 1985, 1310; M. Braga, Inorg. Chem., 1985, 24, 2702.
[18b]G. Hunter et al., J. Chem. Soc. Dalton Trans., 1987, 1545.

Of course, the Lewis basicities of the PX_3 ligands vary considerably,[19] and not entirely predictably[20] with X. This must be taken into consideration because, as with other classes of ligands, the synergistic relationship between σ donation and π acceptance (regardless of the exact mechanism for the latter) is also a source of ambiguity in understanding this class of ligands.[21]

The extent of both donation from the lone pair on the P atom and back-donation depends on the nature of the groups attached to P. For PH_3 and $P(alkyl)_3$, π-acceptor ability is very low, but it becomes important with more electronegative groups. Analogous PX_3, AsX_3, and SbX_3 compounds differ very little, but the ligands having a nitrogen atom, which lacks π orbitals, cause significantly lower frequencies for the CO vibrations, as indicated by the CO stretching frequencies (cm^{-1}) in the following series of compounds:

$(PCl_3)_3Mo(CO)_3$	2040, 1991
$(AsCl_3)_3Mo(CO)_3$	2031, 1992
$(SbCl_3)_3Mo(CO)_3$	2045, 1991
dien $Mo(CO)_3$	1898, 1758

The pronounced effect of the electronegativity of the groups X is shown by the following CO stretching frequencies

$[(C_2H_5)_3P]_3Mo(CO)_3$	1937, 1841
$[(C_6H_5O)_3P]_3Mo(CO)_3$	1994, 1922
$[Cl_2(C_2H_5O)P]_3Mo(CO)_3$	2027, 1969
$(Cl_3P)_3Mo(CO)_3$	2040, 1991
$(F_3P)_3Mo(CO)_3$	2090, 2055

The most electronegative substituent, F in PF_3, will reduce very substantially the σ-donor character so that there will be less $P \rightarrow M$ electron transfer, and $Md\pi \rightarrow Pd\pi$ transfer should be aided. The result is that PF_3 and CO are quite comparable in their π-bonding capacity.

Attempts to order a large number of PX_3, AsX_3, and SbX_3 ligands according to their net π-accepting capacity have been made using $LNi(CO)_3$ compounds, and to a lesser extent others such as $LCr(CO)_5$. Both the CO stretching frequencies and the ^{13}C chemical shifts of the CO groups have been used as the indicative experimental parameter[22] and the two orderings are in general agreement. Based on these data some of the more common phosphorus li-

[19]T. T. Derencsengi *Inorg. Chem.*, 1981, **20**, 665.

[20]G. M. Bancroft *et al.*, *Inorg. Chem.*, 1986, **25**, 3675.

[21]W. P. Giering *et al.*, *Organometallics*, 1985, **4**, 1981; see also R. V. Honeychuck and W. H. Hersh, *Inorg. Chem.*, 1987, **26**, 1826.

[22]G. M. Bodner *et al.*, *Inorg. Chem.*, 1980, **19**, 1951; T. Bartik *et al.*, *J. Organomet. Chem.*, 1984, **272**, 29.
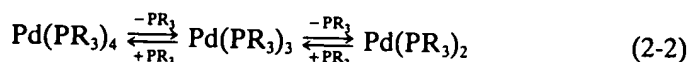
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rtik et al., J. Organomet. Chem.,

gands come out in the following order (As and Sb ligands come very close to the corresponding P ligands):

$$PF_3 > PCl_3 > P(OAr)_3 > P(OR)_3 > P(Ar)_3 > PR(Ar)_2 > PR_2Ar > PR_3$$
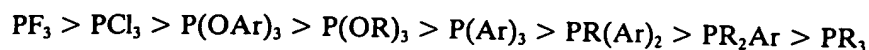
There is also structural evidence to support this general order.[23] For example, in $(PhO)_3PCr(CO)_5$ the P—Cr bond is 0.11 Å shorter than that in $Ph_3PCr(CO)_5$.

Of at least as great importance to the chemistry of PX₃ compounds as the electronic factors are *steric factors*.[24] Indeed these may be more important or even dominant in determining the stereochemistries and structures of compounds. Steric factors also affect rates and equilibria of dissociation reactions such as eq. 2-2 and the propensity of phosphine complexes to undergo oxidative–addition reactions, or form olefin complexes.[25]

$$Pd(PR_3)_4 \underset{+PR_3}{\overset{-PR_3}{\rightleftharpoons}} Pd(PR_3)_3 \underset{+PR_3}{\overset{-PR_3}{\rightleftharpoons}} Pd(PR_3)_2 \qquad (2\text{-}2)$$

The stereochemistry of phosphine ligands is the prime factor in many highly selective catalytic reactions of phosphine complexes, such as hydroformylation and asymmetric hydrogenation (Chapter 28).

The steric requirement of a PX₃ ligand is usually expressed by Tolman's cone angle, θ, as defined below. The cone in question is one that can just enclose the van der Waals surface of all ligand atoms over all rotational orientations about the M—P bond.* Triphenylphosphine has θ = 145° and P(OCH₃)₃ has θ = 107 ± 2°. It might have been expected that compounds with smaller cone angles would be better ligands, but since such compounds
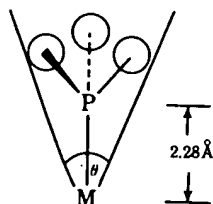
are stronger bases, it is not always easy to distinguish steric from electronic factors although some progress in this respect is being made[24]. However, increasing the cone angle by having bulky groups tends to favor (a) lower coordination numbers, (b) the formation of less sterically crowded isomers, and (c) increased rates and equilibria in dissociative reactions. An example

[23]J. L. Atwood et al., Organometallics, 1985, 4, 867.
[24]C. A. Tolman, Chem. Rev., 1977, 77, 313; see also W. P. Giering et al., Organometallics, 1987, 6, 650 for discussion of steric and σ and π electronic effects and their separation.
[25]C. A. Tolman et al., Organometallics, 1983, 2, 1391.
*More sophisticated definitions have been suggested but offer little practical advantage. See, for example, T. Bartik et al., J. Organomet. Chem., 1984, 272, 29.

of the latter effect is provided by the reactions

$$NiL_4 \overset{K}{=} NiL_3 + L$$

where K varies from >1 for L = PPh_3 ($\theta = 145°$) to $<10^{-10}$ for L = $P(OEt)_3$ ($\theta = 109°$).

2-11. Multiple Bonds from Ligands to Metals

The concept of metal-ligand bonds as simple two-electron L $\rightarrow$ M donor bonds has broad applicability. As noted in Sections 2-8 through 2-10 a significant amount of M $\rightarrow$ L π bonding must be superimposed upon this for M—CO, M—NO, and other related ligands. Thus, these metal-ligand bonds have partial π character and bond orders >1 (but <1.5). However, there are many cases in which metal atoms form full double and triple bonds, either to nonmetal atoms (ligands) or to other metal atoms. The various multiple metal-metal bonds are discussed in Chapter 23.

We are concerned here with bonds of the types[26]

$$M{=}O \qquad M{=}S \qquad M{=}CR_2 \qquad M{=}NR \qquad M{\equiv}CR \qquad M{\equiv}N$$

as well as some M—X—M systems where multiple bond character is present in the M—X—M bonds. In all of these cases, overlap between ligand atom $p\pi$ orbitals and metal atom $d\pi$ orbitals must be invoked to account for bonding in addition to the M—X σ bonds.

M=O and M—O—M Bonds.   The M=O bonds are extremely numerous. In general, the distances are very short, namely, 1.5 to 1.8 Å depending on oxidation numbers, other ligands, and so on. In many cases the bond order is probably significantly >2 because there are two filled $p\pi$ orbitals on the oxygen atom, both of which can engage in bonding to appropriately directed $d\pi$ orbitals on the metal atom, as shown in (2-XXV). There is no reason why, in many cases, that both of these interactions cannot proceed to the point where the sum of the two partial dative π bonds exceeds the bonding that would be provided by just one such interaction at its full extent. Thus, when a double bond, M=O is written, this should be regarded as a formalism and not an accurate specification of bond order.

(2-XXV)
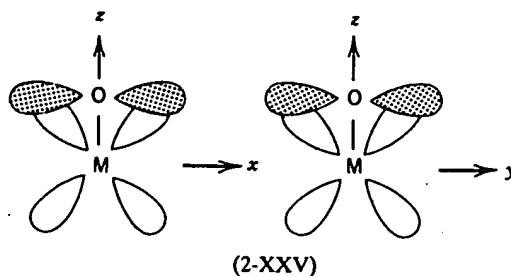
[26]W. A. Herrmann, *Angew. Chem. Int. Ed. Engl.*, 1986, 25, 56.

IPLES

ns

L

45°) to <10^{-10} for L = P(OEt)$_3$

ls

le two-electron L → M donor
sections 2-8 through 2-10 a sig-
be superimposed upon this for
Thus, these metal-ligand bonds
(but <1.5). However, there are
double and triple bonds, either
al atoms. The various multiple
23.

types[26]

JR   M≡CR   M≡N

ltiple bond character is present
·, overlap between ligand atom
invoked to account for bonding

O bonds are extremely numer-
amely, 1.5 to 1.8 Å depending
1. In many cases the bond order
e two filled $p\pi$ orbitals on the
nding to appropriately directed
(2-XXV). There is no reason
actions cannot proceed to the
: π bonds exceeds the bonding
raction at its full extent. Thus,
uld be regarded as a formalism
er.

→ y

25, 56.
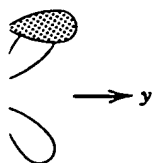
There are also many examples of linear M—O—M units, and in these more delocalized π bonding occurs. The [Cl$_5$MOMCl$_5$]$^{n-}$ ions provide straightforward examples.[27] It may be assumed that by using a pair of sp hybrid orbitals on the oxygen atom a linear pair of M—O—M σ bonds is formed. There are then two orthogonal, occupied $p\pi$ orbitals on the oxygen atom that can interact with suitable metal $d\pi$ orbitals. Now, however, there is a total of four such $d\pi$ orbitals and two sets of π interactions (2-XXVI) (one in the xz plane and the other just like it in the yz plane) will be established. With both of the two components of the E_u orbital occupied, there is a total of four σ electrons and four π electrons, and thus each M—O bond may be assigned (formally) a bond order of 2. This is consistent with the occurrence of M—O distances in the range of 1.75 to 1.90 Å for various M—O—M systems.[27]

E_u

E_u^*

B
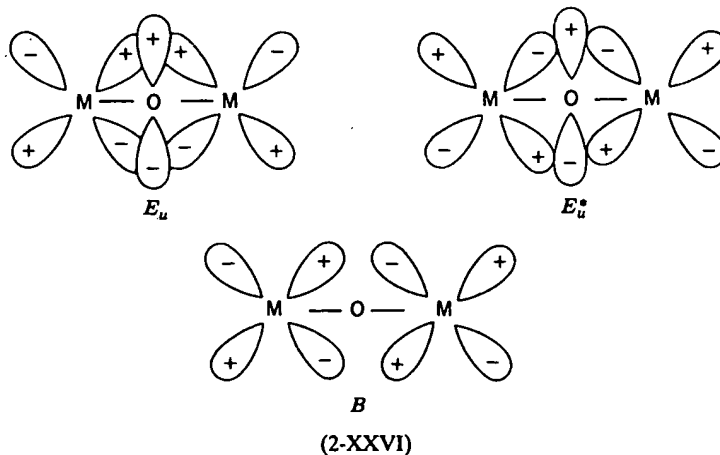
(2-XXVI)

Metal–Nitrogen Multiple Bonds.[28] As with oxygen there are two types, M≡N and M=N=M, but the former show a pronounced tendency towards association, either into linear chains (2-XXVII) or cycles (2-XVIII) as found in MoNCl$_3$. For discussion of chemistry, see Section 10-18.

(2-XXVII)   (2-XXVIII)
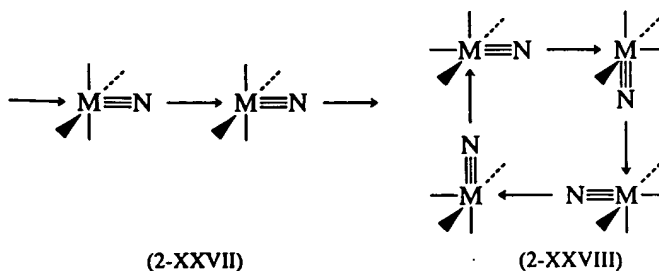
[27]F. A. Cotton and R. C. Najjar, *Inorg. Chem.*, 1981, **20**, 1866.
[28]R. Hoffmann *et al.*, *J. Am. Chem. Soc.*, 1986, **108**, 5381.

The types of orbital overlaps entailed in the formation of $M \equiv N$ and $M = N = M$ bonds are entirely analogous to those already discussed for the oxo cases. As full triple bonds, the $M \equiv N$ linkages are generally very short (e.g., 1.66 Å in $MoCl_4N^-$, and 1.58 Å in $ReCl_4N$), but the bonds ion $M = N = M$ systems are longer (~1.85 Å).

Metal to nitrogen double bonds[29] are found in the $M = NR$ compounds, sometimes called nitrenes (by analogy to carbenes), but better designated metal imides. Here the bonding can be described in very conventional terms with one σ bond, one π bond and a lone pair of electrons, as in (2-XXIX).

(2 = XXIX)
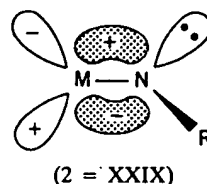
$M = CR_2$ and $M \equiv CR$ bonds. These play an enormous role in organo-metallic chemistry and will be discussed at length in Chapter 25. The nature of the M to C bonding is very much dependent on the nature of M and R.[30] At one extreme there are compounds in which M is in a high valence state and the R group(s) not of π-donor character. In these cases, the bonds are comparable to those just discussed for $M = NR$ and $M \equiv N$. For these types of compounds, the terms *alkylidene* ($M = CR_2$) and *alkylidyne* ($M \equiv CR$) have been favored. On the other hand, when the metal is in a low valence state and the substituents on carbon are π donors, the M—C bonds are *not* full double or triple bonds and the systems are rendered stable by the migration of charge from the substituents (such as OR or NR) on the carbon atom, as shown in resonance terms in (2-XXX). In these types of compounds it is customary to use the terms *carbene complex* and *carbyne complex*. The chemistry is qualitatively different for the two classes of each type (i.e., MCR_2 and MCR) of compound, as will be discussed in Chapter 25.

(2-XXX)
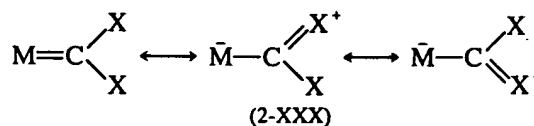
Heavier Ligand Atoms. We have just discussed the formation of M—X multiple bonds for the principal cases where X is an element from the first short period, namely, C, N, or O. It is to be noted that recently analogues for some of these, in which the heavier elements, Si, Ge, P, As, S, and Se occur, have been prepared, and doubtless this development will continue rapidly. As a first approximation the M—X bonding to the heavier X atoms

[29] W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31**, 123.
[30] E. A. Carter and W. A. Goddard, III, *J. Am. Chem. Soc.*, 1986, **108**, 4746.

ation of M≡N and M=N=M
discussed for the oxo cases. As
erally very short (e.g., 1.66 Å
bonds ion M=N=M systems

d in the M=NR compounds,
benes), but better designated
ed in very conventional terms
of electrons, as in (2-XXIX).

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R

an enormous role in organo-
gth in Chapter 25. The nature
t on the nature of M and R.[30]
h M is in a high valence state
In these cases, the bonds are
R and M≡N. For these types
and *alkylidyne* (M≡CR) have
netal is in a low valence state
the M—C bonds are *not* full
idered stable by the migration
r NR) on the carbon atom, as
iese types of compounds it is
d *carbyne complex*. The chem-
s of each type (i.e., MCR$_2$ and
hapter 25.

→ M̄—C⟨$_{X^+}^{X}$
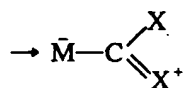
ussed the formation of M—X
X is an element from the first
noted that recently analogues
:nts, Si, Ge, P, As, S, and Se
iis development will continue
onding to the heavier X atoms

, 1980, **31**, 123.
oc., 1986, **108**, 4746.

can be described in the same ways as for the light X atoms, but it is possible
that outer d orbitals may make some contribution for the heavier X atoms.
The greater size of the heavier elements may also be important in some cases.
Whatever the reasons, compounds such as linear $(C_5Me_5)(CO)_2$ Mn=Ge=
$Mn(CO)_2(C_5Me_5)$ and bent $(C_5Me_5)(CO)_2Mn=Te=Mn(CO)_2(C_5Me_5)$
have no C or O analogues; M=C=M bonds are found in some porphyrin
complexes however (Section 8-9).

Another type of linkage formed only by the heavier elements is displayed
by the compounds $Cp(CO)_2CrXCr(CO)_2Cp$, where X = S, Se but not O.
The very short bonds (e.g., 2.20 Å for Cr—Se), together with other consid-
erations, have been taken to imply that Cr≡X triple bonds exist.

π COMPLEXES OF UNSATURATED ORGANIC MOLECULES

Molecules that have multiple bonds (C=C, C≡C, C=O, C=N, S=O,
N=O, etc.) can form what are called π *complexes* with transition metals.
The chemistry of these is discussed in detail in Chapter 26.

2-12. Alkenes and Alkynes

The most important π complexes are those of compounds with C=C bonds.
The earliest known organotransition metal complex was discovered by W. C.
Zeise in Copenhagen in about 1827, but the true constitution was not rec-
ognized until the 1950s. Zeise's salt, $K[Pt(C_2H_4)Cl_3]$, has ethylene bound to
Pt as shown in Fig. 2-9a.

The key point is that the C=C axis of the coordinated alkene is perpen-
dicular to one of the expected bond directions from the metal. The expected
line of a bond orbital from the metal strikes the C=C bond at its midpoint
(though for unsymmetrical alkenes, this need *not* be so).

Figure 2-9 shows several other examples of olefin complexes as well as a
comparable dioxygen complex.

The most generally useful description of this type of bonding was developed
for copper–alkene complexes by M. J. S. Dewar and later extended to other
transition metals. Figure 2-10 illustrates the assumption that as with other π-
bonding ligands like CO, there are *two* components to the total bonding: (*a*)
overlap of the π-electron density of the olefin with a σ-type acceptor orbital
on the metal atom and (*b*) a "back-bond" resulting from flow of electron
density from filled metal d_{xz} or other $d\pi-p\pi$ hybrid orbitals into *antibonding*
orbitals on the carbon atoms. This view is thus similar to that discussed for
the bonding of carbon monoxide and similar weakly basic ligands and implies
the retention of appreciable "double-bond" character in the olefin. Of course,
the donation of π-bonding electrons to the metal σ orbital and the introduction
of electrons into the π-antibonding orbital both weaken the π bonding in the
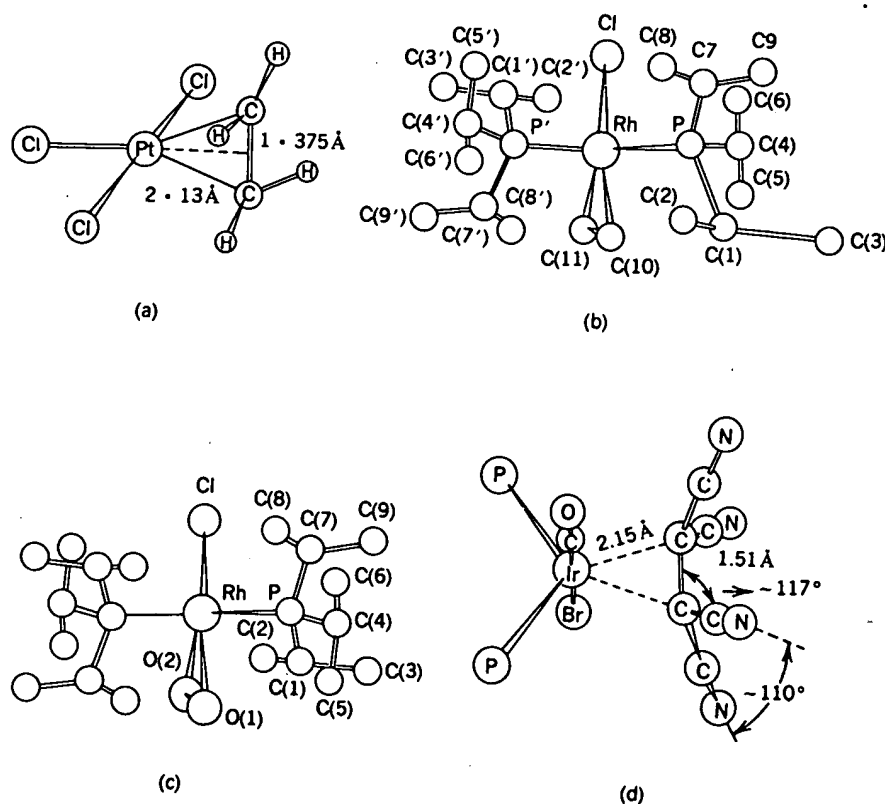
(a)

(b)

(c)

(d)

FIG. 2-9. (a) The structure of the ion in Zeise's salt. (b,c) The structures of ethylene and oxygen complexes, *trans*-RhClL(PPr₃)₂. (d) The structure of the tetracyanoethylene complex IrBr(CO)[(CN)₂C=C(CN)₂](PPh₃)₂.
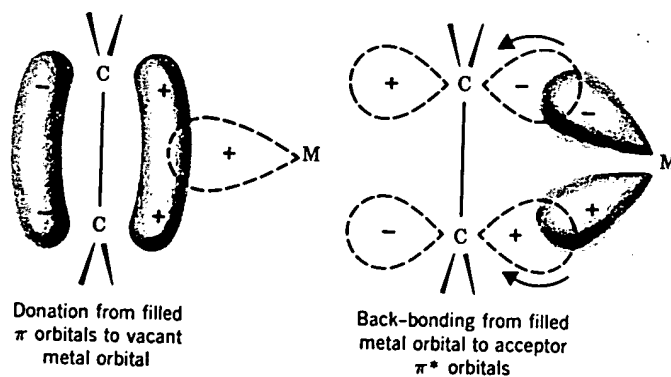

Donation from filled
π orbitals to vacant
metal orbital

Back-bonding from filled
metal orbital to acceptor
π* orbitals

FIG. 2-10. The molecular orbital view of alkene–metal bonding according to Dewar.

72
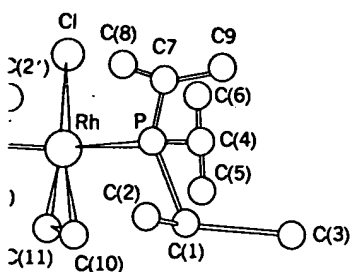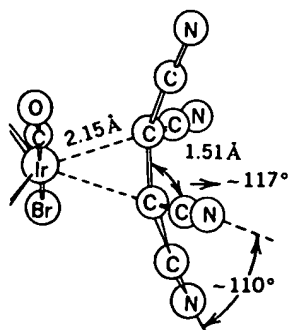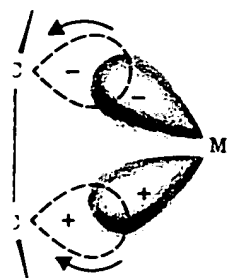
olefin, and in every case except the anion of Zeise's salt there is significant lengthening of the olefin C—C bond.

The important qualitative idea about metal–olefin bonding is that the bonding has dual character. There is donation of those electrons initially forming the C—C π bond into a metal orbital of suitable symmetry, and there is donation of electrons from filled metal orbitals of suitable symmetry back into the π-antibonding orbitals of the olefin. As in the CO case, the two components are synergically related. As one component increases, it tends to promote an increase in the other. On both theoretical and experimental grounds, it appears that the metal–alkene bond is essentially electroneutral, with donation and back-acceptance approximately balanced.

Although, as we have seen, the C—C axis of ethylene is perpendicular to the plane of the square coordination for Zeise's salt and other, similar complexes [Fig. 2-9(a) and (b)], this is not strongly demanded by the bonding. There is also a metal $d\pi$ orbital *in the plane,* and it too can interact with the olefin $p\pi^*$ orbital as shown in Fig. 2-10; the difference in stability between the perpendicular and in-plane orientations is thus not great on a bonding basis (although in-plane bonding is weaker) and may be mainly steric in origin. In any event, measurements of the barrier to rotation[31] of the olefin about an axis defined by a line from the metal atom to the midpoint of the olefin have given results of only 40–70 kJ mol^{-1} and there is one case where the in-plane orientation is found[32].

In complexes containing tetracyanoethylene (Fig. 2-9d) or $F_2C=CF_2$ the C—C bond is about as long as a normal single bond and the angles within the $C_2(CN)_4$ or C_2F_4 ligand suggest that the carbon atoms bound to the metal approach tetrahedral hybridization. Indeed, it is possible to formulate the bonding as involving two normal 2c-2e metal–carbon bonds in a metallacycle (2-XXXIa) with approximately sp^3 hybridized carbon. A number of other molecules that have multiple bonds and can be bound to metals in the η^2 fashion can be regarded as forming metallacycles (2-XXXIb) through (2-XXXIe).

(b)

(d)

...e structures of ethylene and oxygen ...the tetracyanoethylene complex

...g from filled ...l to acceptor rbitals

bonding according to Dewar.

(2-XXXIa)   (2-XXXIb)   (2-XXXIc)   (2-XXXId)   (2-XXXIe)
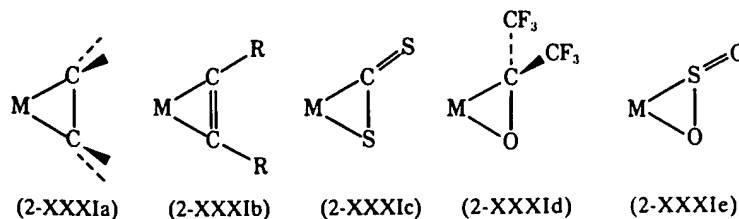
[31]S. Miya and K. Saito, *Inorg. Chem.*, 1981, **20**, 287.

[32]N. Kasai *et al., J. Am. Chem. Soc.*, 1983, **105**, 2482; M. F. Rettig *et al., Organometallics*, 1987, **6**, 1211.

Actually, the metallacycle view and the π-donor view are neither incompatible nor mutually exclusive but are complementary, with a smooth gradation of one description into the other. The one to be preferred in any given case depends on the extent to which the double bond of the ligand has been reduced to a single bond. From a formal point of view, however, the metallacycle view entails a problem with oxidation state. For example, a compound such as $Ni(C_2F_4)(CO)_3$ could be regarded as a nickel(II) rather than a nickel(0) complex. Clearly, in a compound such as $Pt(C_2H_4)_3$, it would be absurd to propose Pt^{VI}. It is best to regard molecules bound sideways as neutral ligands that do not alter the formal oxidation state.

Conjugated Alkenes. When two or more conjugated double bonds are engaged in bonding to a metal atom the interactions become more complex, though qualitatively the two types of basic, synergic components are involved. The case of the 1,3-butadiene unit is an important one and shows why it would be a drastic oversimplification to treat such cases as simply collections of separate monoolefin–metal interactions.

Two extreme formal representations of the bonding of 1,3-butadiene to a metal atom are possible (Fig. 2-11). The structure (b) would imply that bonds 1–2 and 3–4 should be longer than bond 2–3. In $C_4H_6Fe(CO)_3$ the bond lengths are approximately the same and ^{13}C—H coupling constants in the nmr spectra indicate that the hybridization at carbon still approximates to sp^2. However, in some other compounds of conjugated cyclic alkenes, the pattern is of the long–short–long type, indicating some contribution from this extreme structure.

(a)   (b)
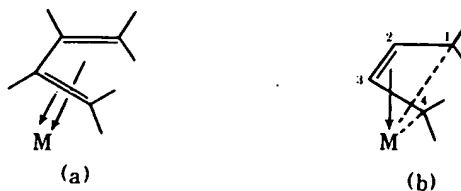
FIG. 2-11. Two extreme formal representations of the bonding of a 1,3-butadiene group to a metal atom: (a) implies that there are two more or less independent monoolefin metal interactions; (b) depicts σ bonds to C-1 and C-4 coupled with a monoolefin metal interaction to C-2 and C-3.

Alkynes. The presence of two mutually perpendicular π bonds in an alkyne makes for considerably more varied and complicated ligand behavior than that shown by alkenes. There is, of course, the simple use of one π bond and the associated π^* orbital in exactly the same way as found in olefin complexes. This results in a lengthening of the C—C distance and a marked deviation from linearity. Typical results are shown schematically in Fig. 2-12(a).

An alkyne can also behave as a formal four-electron donor to one metal atom. In addition to the type of interaction just discussed, the other pair of π electrons may be partially donated to a metal $d\pi$ orbital lying perpendicular

: π-donor view are neither incom-
mplementary, with a smooth gra-
ie one to be preferred in any given
ouble bond of the ligand has been
oint of view, however, the metal-
n state. For example, a compound
a nickel(II) rather than a nickel(0)
$Pt(C_2H_4)_3$, it would be absurd to
bound sideways as neutral ligands
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ore conjugated double bonds are
eractions become more complex,
ynergic components are involved.
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he bonding of 1,3-butadiene to a
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2–3. In $C_4H_6Fe(CO)_3$ the bond
C—H coupling constants in the
at carbon still approximates to
f conjugated cyclic alkenes, the
iting some contribution from this

(b)
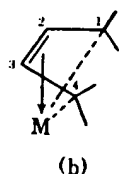
: bonding of a 1,3-butadiene group to a
ss independent monoolefin metal inter-
th a monoolefin metal interaction to C-

y perpendicular π bonds in an
ind complicated ligand behavior
se, the simple use of one π bond
e same way as found in olefin
ie C—C distance and a marked
e shown schematically in Fig.

ur-electron donor to one metal
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il dπ orbital lying perpendicular
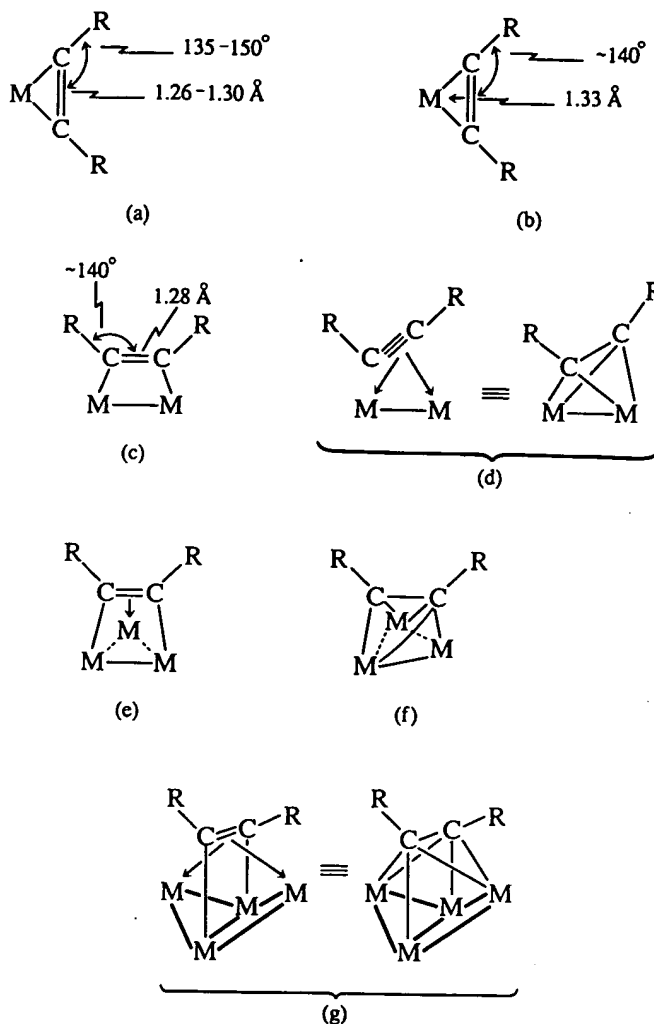
FIG. 2-12. Important modes of ligation of alkynes to single metal atoms and clusters of two, three, and four metal atoms.

to the plane of the three-membered M⟨C—C ring. Again, a synergistic back-donation may also occur if there is a filled d orbital perpendicular to *both* of those already used. This is shown in Fig. 2-13. This typically leads to even greater lengthening of the C—C distance. Figure 2-12(b) shows typical dimensions and indicates how an additional arrow is used to represent this four-electron bonding.
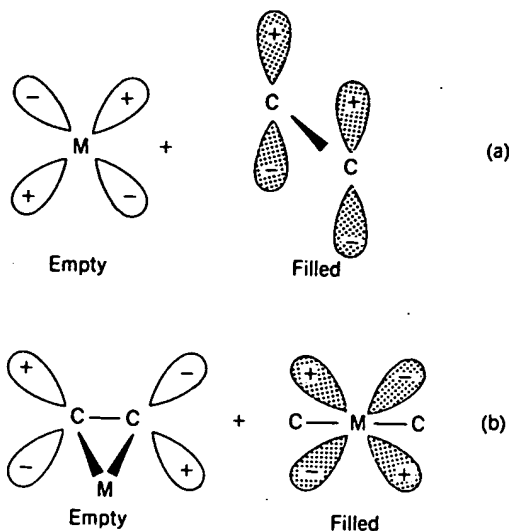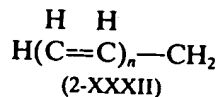
FIG. 2-13. The orbitals employed in the second synergic alkyne-to-metal bond.

When acting as a ligand toward two or more metal atoms, alkynes have a large repertoire of roles. With respect to a dimetal unit, there are two major types of structures, both describable as η^2, μ_2; they are shown in Fig. 2-12(c) and (d). In the planar structure of Fig. 2-12(c), the alkyne, is a two-electron donor. In structure (d), which is a distorted tetrahedral shape, the alkyne is a four-electron donor. The bonding in Fig. 2-12(d) can be envisioned as donation of one pair of π electrons to each metal atom (with appropriate back-donation) or as the formation of two single bonds to each metal atom. The latter view is certainly too extreme since the C—C distances in these cases are in the range 1.30 to 1.35 Å.

With trinuclear sets of metal atoms there are again two principal geometries, Fig. 2-12(e) and (f), in each of which the alkyne is a formal four-electron donor. Finally, we note that towards a tetranuclear set of metal atoms, the geometry shown in Fig. 2-12(g), where the metal atoms have the nonplanar "butterfly" arrangement is common. Here, again, the alkyne is a formal four-electron donor.

2-13. Enyl Ligands

Groups of the formal type 2-XXXII can interact with a metal atom so as to serve as $(2n + 1)$-electron ligands. The two cases of greatest interest are the allyl and pentadienyl groups.

$$\begin{array}{cc} \text{H} & \text{H} \\ \end{array}$$
$$\text{H(C=C)}_n\text{—CH}_2$$
$$\text{(2-XXXII)}$$

The allyl system displays both η^1 (also often denoted σ behavior) (2-XXXIIIa) and η^3 behavior, (2-XXXIIIb). Note that (1) the η^3-allyl group is a three-electron donor, and (2) the hydrogen atoms of the methylene groups are not equivalent. There are syn-(H_A) and anti-(H_B) protons that can be distinguished by nmr. Many allyls show nonrigid behavior in solution (Section 29-15).

η^1 or σ-Allyl
(2-XXXIIIa)

η^3 or π-Allyl
(2-XXXIIIb)
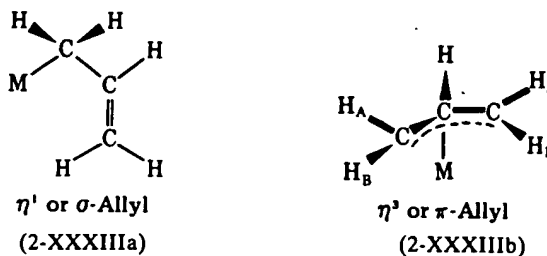
The η^5-pentadienyl ligand[33], as a five-electron donor in its semicircular, delocalised form represented schematically in 2-XXXIV is capable of forming a variety of metal complexes, including a so-called "open" ferrocene, $(C_5H_7)_2Fe$.

(2-XXXIV)
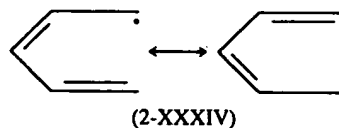
It may also be noted that η^3-allyl and η^5-pentadienyl units are often found within rings, especially six-membered rings, namely,

η-1-3-Cyclohexenyl   allylic

η-1-5-Cyclohexadienyl   dienylic
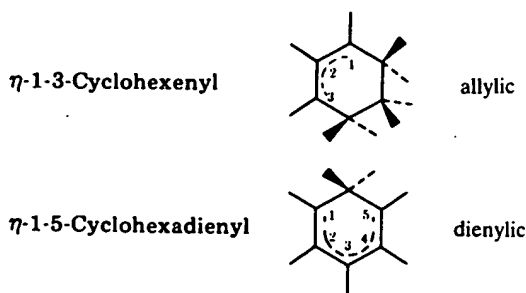
2-14. Aromatic Ring Systems

Just as the π electrons of alkenes can interact with metal d orbitals, so can certain of the delocalized π-electron ring systems of aromatic molecules overlap with d_{xz} and d_{yz} metal orbitals.

The first example of this type of complex was the molecule $Fe(C_5H_5)_2$, now

[33]R. D. Ernst, Struct. Bonding (Berlin), 1984, 57, 1–53.

(a)

—C   (b)

:rgic alkyne-to-metal bond.

netal atoms, alkynes have a
al unit, there are two major
ey are shown in Fig. 2-12(c)
he alkyne, is a two-electron
ihedral shape, the alkyne is
2(d) can be envisioned as
tal atom (with appropriate
bonds to each metal atom.
ie C—C distances in these

again two principal geome-
/ne is a formal four-electron
:ar set of metal atoms, the
atoms have the nonplanar
the alkyne is a formal four-

with a metal atom so as to
of greatest interest are the

known as *ferrocene*, in which the 6π-electron system of the ion $C_5H_5^-$ is bound to the metal. Other aromatic systems with the "magic numbers" of 2, 6, and 10 for the aromatic electronic configuration are the carbocycles:
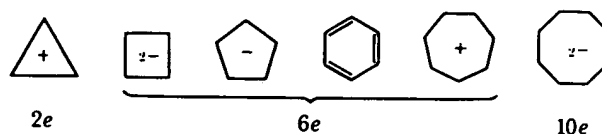

The C_5H_5, C_6H_6, and C_8H_8 rings are the most common in complexes, but the C_7H_7 and C_4H_4 systems also occur frequently. It should also be noted that for purposes of electron counting the ring system and the metal atom may be considered as neutral. For example, the total of 18 electrons in ferrocene can be regarded as 5 per C_5H_5 ring plus 8 from Fe.

Compounds are known that have only π-bonded rings such as ferrocene (2-XXXV), dibenzenechromium (2-XXXVI), or $(C_8H_8)_2U$ (2-XXXVII), but

(2-XXXV)   (2-XXXVI)   (2-XXXVII)
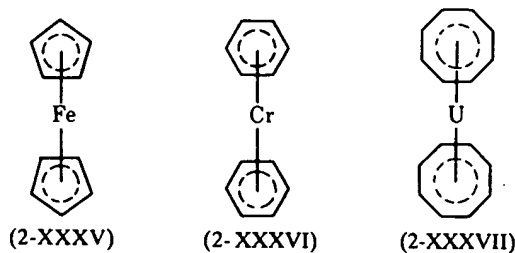
there are many compounds with one ring and other ligands such as halogens, CO, RNC, and R_3P. Examples are η-$C_5H_5Mn(CO)_3$ and η-$C_5H_5Fe(CO)_2Cl$. The symbol η is used to signify that all carbon atoms of the ring are bonded to the metal atom. There are also molecules in which two different types of arene ring are present, such that the total number of π electrons they provide, plus those possessed by the metal atom itself, add to 18. For example, in (2-XXXVIII), there are five π electrons from C_5H_5, four from C_4R_4, and nine from Co. Similarly, we have $(\eta$-$C_5H_5)(\eta$-$C_6H_6)Mn$.

It is also possible for heterocyclic arene rings to form complexes, examples being $(\eta$-$C_4H_4N)Mn(CO)_3$, $(\eta$-$C_4H_4S)Cr(CO)_3$, $(\eta$-$C_5H_5)(\eta$-$C_4H_4N)Fe$, $(\eta$-$C_5H_5)$-$(\eta$-$C_4H_4P)Fe$, and (2-XXXIX).
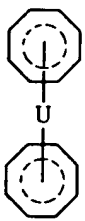

(2-XXXVIII)   (2-XXXIX)
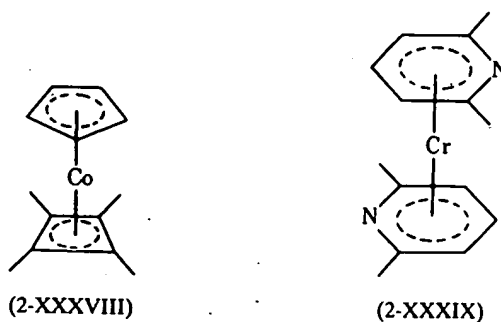
ystem of the ion $C_5H_5^-$ is bound
"magic numbers" of 2, 6, and
re the carbocycles:

$$\boxed{+} \quad \boxed{2-}$$

10e

common in complexes, but the
. It should also be noted that
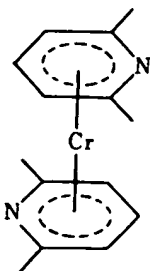stem and the metal atom may
al of 18 electrons in ferrocene
n Fe.

onded rings such as ferrocene
or $(C_8H_8)_2U$ (2-XXXVII), but

(2-XXXVII)

other ligands such as halogens,
(CO)₃ and η-$C_5H_5Fe(CO)_2Cl$.
atoms of the ring are bonded
1 which two different types of
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add to 18. For example, in (2-
H₅, four from C_4R_4, and nine
Mn.

gs to form complexes, exam-
(CO)₃, (η-C_5H_5)(η-C_4H_4N)Fe,

(2-XXXIX)

The basic qualitative features of the bonding in ferrocene are well understood, and will serve to illustrate the basic principles for all $(\eta\text{-}C_nH_n)M$ bonding, although for $(C_8H_8)M$ systems there are a few additional points that are covered later.

The discussion of bonding does not depend critically on whether the preferred rotational orientation of the rings (see Fig. 2-14) in an $(\eta\text{-}C_5H_5)_2M$ compound is staggered (D_{5d}) or eclipsed (D_{5h}); nor is that question unequivocally settled. It is experimentally certain that in ferrocenes the barrier to rotation is only about 8 to 20 kJ mol^{-1}[*]. The eclipsed configuration may be the more stable, but in condensed phases, especially crystals, where there are intermolecular energies of the same or greater magnitude than the barrier, either configuration may be found.

The bonding is best treated in the linear combination of atomic orbitals (LCAO–MO) approximation. A semiquantitative energy level diagram is given in Fig. 2-15. Each C_5H_5 ring, taken as a regular pentagon, has five π MO's, one strongly bonding (a), a degenerate pair that are weakly bonding (e_1), and a degenerate pair that are markedly antibonding (e_2), as shown in Fig. 2-16. The pair of rings taken together then has ten π orbitals and, if D_{5d} symmetry is assumed, so that there is a center of symmetry in the $(\eta\text{-}C_5H_5)_2M$ molecule, there will be centrosymmetric (g) and antisymmetric (u) combinations. This is the origin of the set of orbitals shown on the left of Fig. 2-15. On the right are the valence shell $(3d, 4s, 4p)$ orbitals of the iron atom. In the center are the MO's formed when the ring π orbitals and the valence orbitals of the iron atom interact.

For $(\eta\text{-}C_5H_5)_2Fe$, there are 18 valence electrons to be accommodated: 5 π-electrons from each C_5H_5 ring and 8 valence shell electrons from the iron atom. It will be seen that the pattern of MO's is such that there are exactly 9 bonding or nonbonding MO's and 10 antibonding ones. Hence the 18 electrons can just fill the bonding and nonbonding MO's, giving a closed configuration. Since the occupied orbitals are either of a type (which are each symmetric around the 5-fold molecular axis) or they are *pairs* of e_1 or e_2 type, which are also, *in pairs*, symmetrical about the axis, no intrinsic barrier to
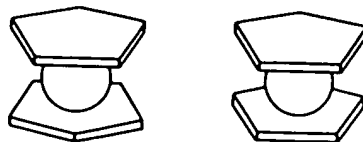
FIG. 2-14. Staggered and eclipsed configurations of an $(\eta\text{-}C_5H_5)_2M$ compound. In crystalline ferrocene there are molecules of different orientations randomly distributed throughout the crystal (P. Seiler and J. D. Dunitz, *Acta Cryst.*, 1979, **B35**, 1068). Also, the H atoms of the rings are bent towards the metal (F. Takasagawa and J. F. Koetzle, *Acta Cryst.*, 1979, **B35**, 1074).

*There are similar values for the rotation of rings in arene compounds; see J. Howard *et al.*, *J. Chem. Soc. Dalton Trans.*, 1982, 967, 977.
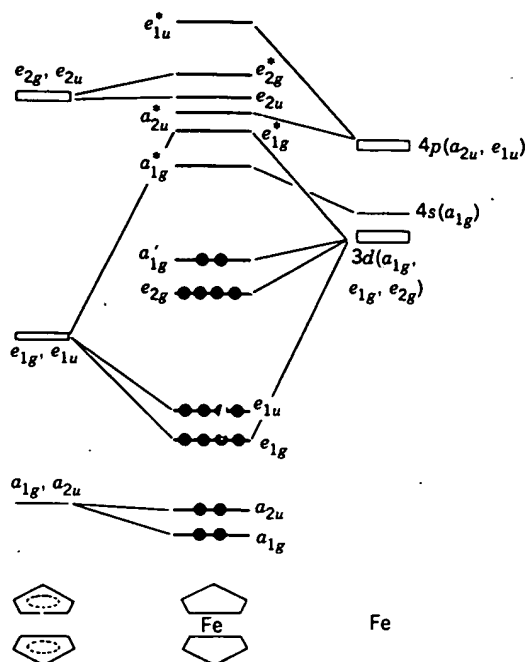
FIG. 2-15. An approximate MO diagram for ferrocene. Different workers often disagree about the exact order of the MO's; the order shown here, especially for the antibonding MO's, may be incorrect in detail, but the general pattern is widely accepted.

internal rotation is predicted. The very low barriers observed may be attributed to van der Waals forces directly between the rings.

Figure 2-15 indicates that among the principal bonding interactions is that giving rise to the strongly bonding e_{1g} and strongly antibonding e_{1g}^* orbitals. To give one concrete example of how ring and metal orbitals overlap, the nature of this particular important interaction is illustrated in Fig. 2-17. This particular interaction is in general the most important single one because the directional properties of the e_1-type d orbitals (d_{xz}, d_{yz}) give an excellent overlap with the e_1-type ring π orbitals, as Fig. 2-17 shows.

Systems containing only one η-C_5H_5 ring include (η-C_5H_5)Mn(CO)$_3$, (η-C_5H_5)Co(CO)$_2$, (η-C_5H_5)NiNO, and (η-C_5H_5)CuPR$_3$. The ring-to-metal bonding in these cases can be accounted for by a conceptually simple modification of the picture given previously for (η-C_5H_5)$_2$M systems. In each case a principal axis of symmetry can be chosen so as to pass through the metal atom and intersect the ring plane perpendicularly at the ring center; in other words, the C_5H_5M group is a pentagonal pyramid, symmetry C_{5v}. The single ring may then be considered to interact with the various metal orbitals in about the same way as do each of the rings in the sandwich system. The only difference is that opposite to this single ring is a different set of ligands which

4p(a_{2u}, e_{1u})

4s(a_{1g})

3d(a_{1g}, e_{1g}, e_{2g})

Fe
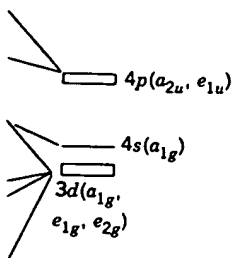
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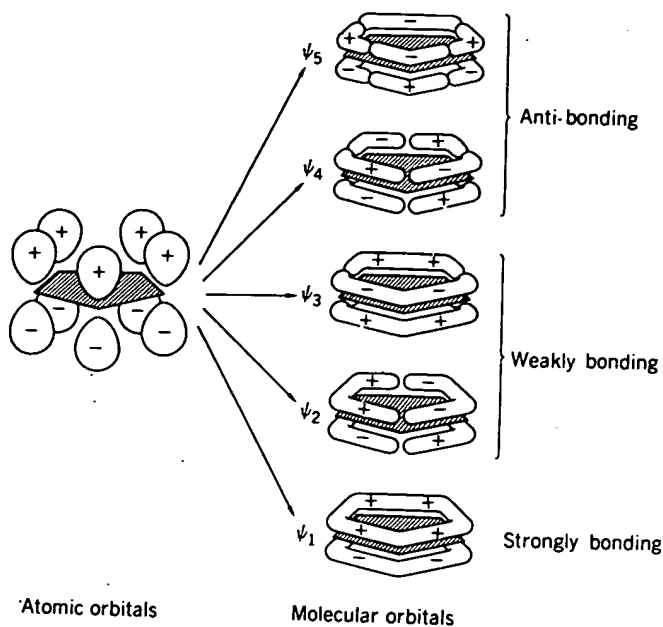
FIG. 2.16. The π molecular orbitals formed from the set of $p\pi$ orbitals of the C_5H_5 ring.
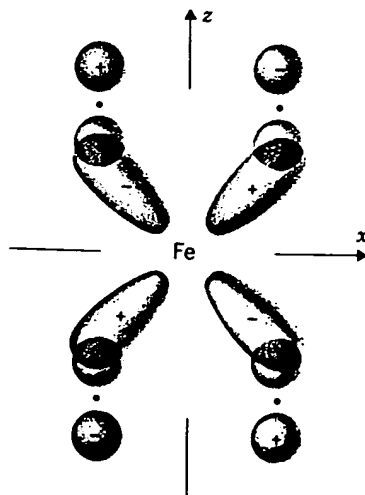
FIG. 2.17. Overlapping of one of the e_1-type d orbitals d_{xz} with an e_1-type π orbital to give a delocalized metal-ring bond: cross-sectional view taken in the xz plane.

interact with the opposite lobes of, for example, the de_1 orbitals, to form their own appropriate bonds to the metal atom.

The MO picture of ring-to-metal bonding just given for ferrocene is *qualitatively* but *not quantitatively* applicable to other $(\eta\text{-}C_5H_5)_2M$ compounds, and with obvious modifications, to other $(\eta\text{-arene})_2M$ molecules. Relative orbital energies can and do change as the metal is changed. Ferrocene itself has been treated by very elaborate MO calculations, and at the other extreme a ligand field model has also been applied to the $(\eta\text{-}C_5H_5)_2M$ compounds generally. Although it is clearly unrealistic to treat the bonding in these systems as electrostatic (i.e., M^{2+} and two negatively charged rings), this approach is of some utility in interpreting electronic absorption spectra.

It must also be noted that not all $(C_5H_5)_2M$ compounds are as simple structurally or electronically as might naively be expected. Those involving titanium and niobium have complex binuclear structures, as described in detail under the chemistry of these elements. In the case of $(\eta\text{-}C_5H_5)_2Ni$ there are two electrons in excess of those required for an 18-electron configuration; nonetheless, the molecule appears to have a structure with parallel rings and the two additional electrons have been assigned to the e_{1g}^* orbitals where they are appreciably delocalized onto the rings.

$(C_5H_5)_2Mn$ has a structure (Fig. 2-18) in which there are no discrete molecules until a transition occurs at 159°C, where it becomes isomorphous with ferrocene. However, there are five unpaired d electrons and the Mn to ring bonding is mainly ionic. $(CH_3C_5H_4)_2Mn(g)$ at 25°C is a roughly 2 to 1 mixture of ionic (high-spin) and covalent (low-spin) molecules with Mn—C distances of 2.42 and 2.14 Å, respectively, while $(C_5Me_5)_2Mn$ is molecular with one unpaired electron.

In many cases the rings are not parallel because additional ligands are present, for example, in $(C_5H_5)_2MX_2$ compounds with M = Ti, Zr, Mo and X = Cl, H, or R, or $(C_5H_5)_2MnPR_3$.[34] Bent molecules are also formed by tin and lead, where there is a stereochemically active lone pair.[35] Finally there

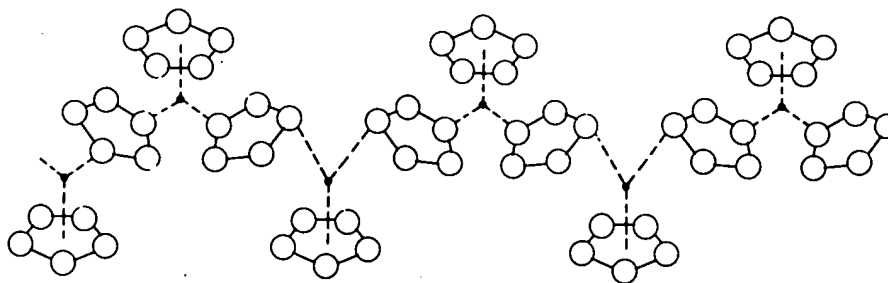FIG. 2.18. The chain structure of $(C_5H_5)_2Mn$ in the low-temperature, antiferromagnetic crystal form.

[34]G. Wilkinson *et al., J. Am. Chem. Soc.,* 1984, **106,** 2033.
[35]A. H. Cowley *et al., J. Am. Chem. Soc.,* 1982, **104,** 4064.

ple, the de_1 orbitals, to form their

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: other $(\eta\text{-}C_5H_5)_2M$ compounds,
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c to treat the bonding in these
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$_5)_2M$ compounds are as simple
ly be expected. Those involving
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d electrons and the Mn to ring
25°C is a roughly 2 to 1 mixture
nolecules with Mn—C distances
$Me_5)_2Mn$ is molecular with one

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active lone pair.[35] Finally there
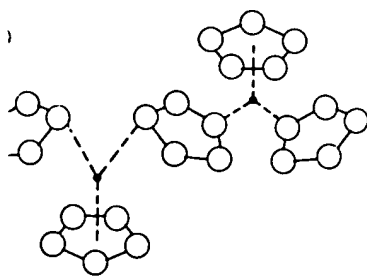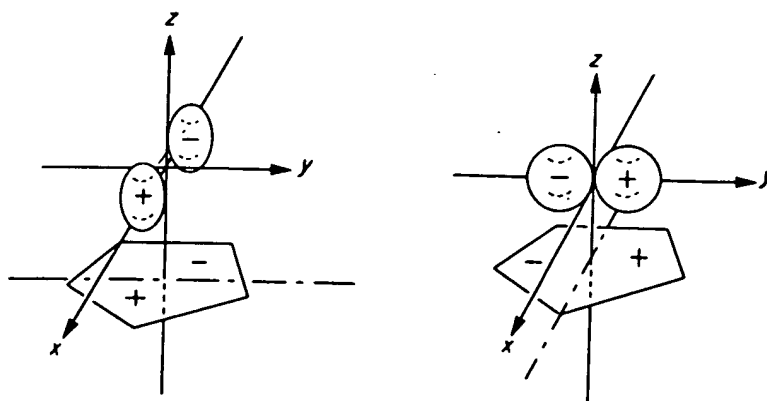
temperature, antiferromagnetic crystal

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64.

FIG. 2.19. Diagrams showing how p_x and p_y orbitals are symmetry adapted to overlap the e_1 π orbitals of a C_5H_5 ring.

can be "slippage" of the metal from the center to one side of the ring, which is probably important in the conversion of η^5 to η^1 species (Section 26-10).[36]

It is also possible to have covalent $(\eta\text{-}C_5H_5)M$ groups even when the metal atom has no valence shell d orbitals, provided it has p orbitals of suitable energy and size. As shown in Fig. 2-19, a pair of p_x and p_y orbitals can overlap with the e_1 π orbitals of C_5H_5 in much the same way as do d_{xz} and d_{yz} orbitals. The C_5H_5In and C_5H_5Tl molecules are the best documented cases of this type of bonding.

Bonding in $(\eta\text{-}C_8H_8)_2M$ Molecules. Although there are a few cases—for example, $(\eta\text{-}C_8H_8)ZrCl_2(THF)$—of one fully octagonal, planar C_8H_8 ring being symmetrically bonded to a d-block metal and it may be safely assumed that only metal d orbitals are used, the $(\eta\text{-}C_8H_8)_2M$ compounds are formed only by metal atoms like uranium and thorium where the participation of f orbitals might reasonably be expected. However, at present, the role of the f orbitals is still not well defined. See Section 21-7 for further discussion and references.

General References

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[x]J. W. Faller *et al.*, *Organometallics*, 1985, **4**, 929; D. L. Lichtenberger *et al.*, *Organometallics*, 1984, **3**, 1614, 1623.